

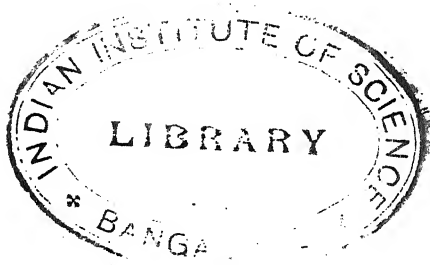
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**BIBLIOGRAPHICAL NOTE.**

*First Edition* . . . . . 1908.  
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## PREFACE TO THE FRENCH EDITION

WHILST perusing the sheets of the technical treatise which MM. P. Dumesny and J. Noyer have asked me to present to the public, I could not help being struck with the progress which chemical science has accomplished in the last thirty years—a progress which leads it, step by step, to explore all parts of the field of human activity, and to bring to each of those parts the measure of knowledge which it requires. At first the preoccupation of men of science was necessarily dominated by theoretical ideas, by verification of hypotheses, and by the building up of a system of doctrines capable of simultaneously satisfying not only the desire which we possess of demonstrating more and more intimately the constitution of matter, but also the need for simplification of the methods of teaching, and for the incessant realisation of fresh progress.

But realism never loses its rights. It was soon perceived that chemistry could not remain confined to the domain of the laboratory, that the problems of life were within its field, and that its scope became enlarged by association with the material works of mankind, by lessening human labour, and, consequently, increasing the riches and the happiness of different nations. Thus it is that we see men of science interest themselves to an ever-increasing extent in agricultural and industrial problems, and the teaching of industrial chemistry develop in all large countries, and so produce engineers capable of not only placing theory and practice in harmony in each industry, but capable also of modifying, of inventing and of sustaining the competition of products by diminishing their cost price.

It is with the same end in view that, alongside purely scientific literature, a need has made itself felt for technical literature, to enlighten not only the young in their arduous



search after knowledge, and not only the manufacturers themselves, but also their assistants, workmen and foremen whose professional skill is by this acquired knowledge relatively increased.

And here again a natural departure was made. It was to those industries which, working on a large scale and handling considerable capital, were—and should have been—able to be the first to make an appeal to the assistance of the man of science that attention was first of all directed. It is now the turn of industries which, occupying a secondary rank, are, nevertheless, of great importance, as much by the riches which they create as the necessity for the products which they place on the market, and *Wood Products, Distillates and Extracts* are of this latter category.

In France, a wooded country, the industrial chemistry of wood employs a great number of hands. The living which is made out of it is a somewhat hard one, since the charcoal which it prepares has to compete, especially on the markets of large towns, with many rivals, as a source of heat and particularly with gas. To maintain their ground, manufacturers have had, and will have, to improve their equipment continually, increase their range of by-products, and increase the value of some of them, of the tar products especially; it is only by a complete knowledge of the properties of the raw materials and its derivatives, and by the application of rational means of control to all parts of the factory, that they will be able to do so.

The industry of tannic extracts is of more recent date; the products which it prepares assume greater and greater importance, since the adoption of rapid methods of tanning has become a necessity in the hide and leather industry; this importance will continue to increase in proportion as chemical science is installed in the tannery in the place of the rule-of-thumb methods which have reigned there far too long. The preparation of these extracts should fulfil certain conditions; it requires an equipment which, to be conducted economically, must be continually supervised. And here again, as in the industry of the chemical derivatives of wood, it is the complete scientific knowledge of his trade which should guide the manufacturer, the foreman and the workman.

The treatise of MM. Dumesny and Noyer is, therefore, a timely one. Written by two practical men, distinguished engineers, who know their subject, their collaboration could only result in the production of a book both scientific and technical, which contains all the instructions necessary for the methodical carrying on of each of the industries within its purview, and which consequently has its distinctive place in the factory laboratory and in the laboratory of the student. I have pleasure in presenting it to the public and to predict for it a deserved success.

E. FLEURENT,

*Docteur ès Sciences,*

*Professeur de Chimie Industrielle au Conservatoire National  
des Arts et Métiers.*

## PREFACE TO THE SECOND EDITION

THERE are several ways of treating wood for the production of useful products, among these being destructive distillation and the preparation of extracts by infusion.

In Part I. of this book the destructive distillation of various kinds of wood is studied in detail, and also the products of such distillation, *e.g.*, charcoal, acetic acid, wood spirit, and wood tar. The methods of purifying these products and preparing from them other useful chemicals is fully described. This section also contains a description of the methods of analysis of the raw and finished products.

Part II. is devoted to a description of the various tanning materials and logwood. The methods of preparing from them concentrated fluid and solid extracts and the machinery and plant used in these industries is very fully dealt with. A considerable amount of information is given as to the effect of impurities in the water on the composition of tanning extracts, and also on the methods of evaporation. The Official Methods of Tannin analysis are given at the end of this section.

The numerous illustrations of plant and the tables of data which are given throughout the book cannot fail to add to its value. Prices are often quoted in the first edition, some of these have been deleted but those still left in the text refer to the year 1908; it was impossible to alter them at present as fixed prices could not be given; they may serve a useful purpose if only for comparison.

Some of the matter in the last edition has been deleted and much new material added. It is the hope of the reviser that the work will have as favourable a reception as the first edition.

H. B. STOCKS.

LONDON, *April*, 1921.



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## PART I

### THE DISTILLATION OF WOOD

#### CHAPTER I

##### INTRODUCTION

THE chemical industries dealing with wood—more especially the dry distillation of wood—have rapidly attained a considerable importance throughout the whole world. Thus in Europe alone the capital invested exceeds a milliard of francs (£40,000,000). Also the area annually occupied by the forests, which serve the pyroligneous industry, in certain countries, can be measured in hundreds of thousands of hectares<sup>1</sup> which annually produce hundreds of thousands of cubic metres of wood.<sup>2</sup> In North America alone whole forests are cleared every year, the wood being used to manufacture the products exported into Europe by the United States. The industrial distillation of wood dates from the year 1798, the first experiments being due to Philip Lebon. Lebon submitted wood to the action of heat in a retort, with the production of various products, and thus created the industry of wood carbonisation, which afterwards made immense progress, especially about the time of the discovery of the coal-tar colours, the manufacture of which required large quantities of acetic acid and methylic alcohol. A new outlet for methylic alcohol was created at a later period, when the present laws in England, France, and Germany regulated the use of wood-spirit for denaturing industrial alcohol. In France are felled every year 250,000 to 300,000 stères<sup>2</sup> of oak, beech, etc.; this enormous amount of timber being out of all proportion to the extent of the annual plantation in French forests there is a constant prejudicial deafforestation of the land, which will be readverted to in a later chapter. Nevertheless, the consumption of methyl alcohol in France greatly exceeds the production in that country, but the exports out of

<sup>1</sup> 1 hectare = 2·47 acres.

<sup>2</sup> A stère or cubic metre being 35 cubic feet and a cord 125 cubic feet; to bring stères to cords multiply by  $\frac{7}{25}$ .

France of acetic acid greatly exceed the imports thereof as the following statistics for 1903 and 1904 show:—

TABLE I.—SHOWING IMPORTS AND EXPORTS OF METHYL ALCOHOL INTO AND OUT OF FRANCE DURING YEARS 1903 AND 1904

French Imports from (1903)	Metric Tons.	French Exports to (1903)	Metric Tons.
Germany . . . . .	232½	Switzerland . . . . .	3½
Belgium . . . . .	348	Other foreign countries . . . . .	½
Other foreign countries . . . . .	190	Free zone . . . . .	8½
		Algeria . . . . .	5½
		Other colonies and protec- torates . . . . .	1½
Net weight . . . . .	770½	Net weight . . . . .	20
Value . . . . .	£32,347	Value . . . . .	£852

1904: French imports, gross weight, 171½ metric tons, value £50,000. 1904: French exports, gross weight, 4½ metric tons, value £1240.

TABLE II.—SHOWING IMPORTS AND EXPORTS OF ACETIC ACID INTO AND OUT OF FRANCE DURING YEAR 1903

French Imports from	Metric Tons.	French Exports to	Metric Tons.
Germany . . . . .	1½	Great Britain . . . . .	16
Belgium . . . . .	3½	Switzerland . . . . .	1½
Other foreign countries . . . . .	½	Spain . . . . .	25½
		Italy . . . . .	13½
		Turkey . . . . .	47½
		Other foreign countries . . . . .	36½
		Algeria . . . . .	15½
		Tunis . . . . .	7½
		Other colonies and protec- torates . . . . .	4½
Net weight . . . . .	4½	Net weight . . . . .	168
Value . . . . .	£47	Value . . . . .	£3,362

1904: French imports, gross weight, 1½ metric tons. 1904: French exports, gross weight, 237 metric tons, value £3960.

On the other hand, Germany shows the greatest production, owing to the development of the chemical industries, which need large quantities of acetic acid. Thus in 1897 Germany treated 400,000 stères of dry wood, which produced 1500 to 2000 metric tons of wood-spirit, 8000 to 10,000 metric tons of acetate of lime, 10,000 metric tons of wood tar, and 44,000 metric tons of wood charcoal. Since 1880 America has exported large quantities of wood-spirit and acetate of lime to European

countries, this exportation having assumed considerable importance during the last ten years. The greater number of American installations, which may be estimated at about a hundred and are syndicated, delivered into Europe in 1901 2500 tons of wood-spirit, the product of 200,000 tons of dry wood.

Up to recently wood-spirit was the only chemical product which exhibited all the properties required in the denaturation of alcohol so as to render it unfit for consumption (undrinkable). In France the proportion of denaturant added to alcohol, *i.e.* 10 per cent. of methyl alcohol containing 25 per cent. of acetone, used up in 1901 more than 440,000 Imperial British gallons of wood-spirit, the value of which exceeds £80,000. On the other hand, Germany, which employs its denaturants in smaller doses, consumes a still larger amount; thus, in such industries as the manufacture of colouring matters, aniline and methyl aniline, special varnishes, etc., its consumption in 1901 was 26,400,000 British Imperial gallons, of which 1,100,000 gallons were for heating apparatus. During that year the quantity of methylic alcohol used by Germany in its different industries, represented a value of about £1,600,000 in spite of its low selling price, which was twenty-four to twenty-eight shillings per 22½ gallons. At the same time the consumption of acetic acid in the colour industry was even greater than that of methylic alcohol.

The products yielded by the destructive distillation of more or less pure cellulose have been investigated by P. Klason, G. V. Heidenstam, and E. Norlin,<sup>1</sup> who used for this purpose cotton and the sulphite cellulose from pine (*Pinus sylvestris*), fir (*Picea excelsa*), birch (*Betula alba*), and red beech (*Fagus sylvatica*). These products were made up into briquettes of specific gravity 1.2 to 1.4, and were heated in a vertical copper cylinder surrounded by three concentric jackets, the vapours evolved passing down the middle jacket and up the inner one. The temperature was carefully regulated and was also measured by thermo-couples. When the temperature of the inner annular space reached 270° C., which required four to five hours, the temperature inside the retort was found to be about 80° C. higher, which is explained by the exothermic reaction taking place by the decomposition of the cellulose. Afterwards the heat was gradually raised to 400° C. in the annular space, the retort temperature being then 380° C.

The composition of the original materials and the percentage yields of the different products are given as follows:—

<sup>1</sup> *Z. angew. Chem.*, 1909, p. 1205.



TABLE III.—YIELD OF PRODUCTS FROM CELLULOSE

		Cellulose from				
		Cotton.	Pine.	Fir.	Birch.	Beech.
Percentage composition of material:—						
Water . . . . .		4.82	5.6	6.44	6.65	7.81
Ash . . . . .		0.13	0.44	0.49	0.49	0.77
Organic matter . . . . .		95.05	93.96	93.07	93.07	91.42
Relative percentages of distillation products:—						
Gases	Charcoal . . . . .	38.82	36.93	34.86	33.39	32.91
	Carbon dioxide . . . . .	10.35	12.83	11.94	11.14	11.96
	Ethylene . . . . .	0.17	0.21	0.19	0.41	0.25
	Carbon monoxide . . . . .	4.15	3.40	3.92	3.49	3.80
	Methane . . . . .	0.27	0.27	0.22	0.47	0.39
Liquids	Methyl alcohol . . . . .	—	traces	0.07	—	0.19
	Acetone . . . . .	0.07	0.08	0.13	0.15	0.26
	Acetic acid . . . . .	1.39	2.18	2.79	3.89	3.50
	Tar . . . . .	4.18	4.85	6.28	9.58	5.23
	Water . . . . .	34.52	34.17	29.99	29.35	31.88
Organic matter in sodium acetate . . . . .		5.14	4.22	8.50	7.72	8.67
Loss . . . . .		0.94	0.86	1.11	0.40	0.93

*Varieties of Wood used in the Wood Charcoal Industry.*—All kinds of wood may be used for distilling; however, according to the products desired and their yield preference is given to one or other variety, and that according to their density. Wood may for this purpose be classified thus: *Very hard*, Hawthorn; *Hard*, Maple, Box, and Wild Cherry; *Moderately hard*, Oak, Plum, Elm; *Slightly hard*, Beech, Hazelnut, Pear, Chestnut; *Soft*, Pine, Spruce, Larch, Birch, Alder, Horse Chestnut; *Very soft*, Limes, Poplars, and the different varieties of Willows. Ordinary woods give more acetic acid than alcohol; woods of the spruce-fir kind yield more tar.

TABLE IV.—AMOUNT OF PRODUCTS YIELDED PER CORD OF WOOD<sup>1</sup>

Class of Wood.	Char. Bushels.	Alcohol. Galls.	Calcium Acetate. Lb.	Tar. Galls.	Wood Oils. Galls.	Turpen- tine. Galls.
Hard Woods . . . . .	40-50	8-12	150-200	8-20	—	—
Resinous Woods . . . . .	25-40	2-4	50-100	30-60	30-60	{ 12-25 <sup>2</sup> 2-10 <sup>3</sup>
Sawdust . . . . .	25-35	2-4	45-75	—	—	—

<sup>1</sup> Veitch, Dep. Agr., U.S.A.<sup>2</sup> Light wood.<sup>3</sup> Sawdust.

*Chemical Phenomena connected with the Carbonisation of Wood.*—The results obtained are quite different according to whether the wood is distilled slowly or rapidly. Thus Violette found that elder wood which yielded 18.9 per cent. of its weight of charcoal by slow distillation only gave 9 per cent. by quick distillation.

TABLE V.—SHOWING THE RESULTS OBTAINED BY SLOW (A) AND QUICK (B) DISTILLATION OF WOOD (SENFFT)

	Charcoal.		Gas.		Distilled Products.		Pyroligneous Acid.		Acetic Acid.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
Hornbeam	25.37	20.47	22.23	31.01	52.04	48.52	47.65	42.97	6.43	5.23
Alder	31.56	21.11	17.91	31.13	50.53	47.76	44.14	40.70	5.77	4.13
Birch	29.24	21.46	19.71	35.56	51.05	42.98	45.59	39.74	5.63	4.43
Rowan	27.84	20.20	20.62	33.40	51.54	46.40	44.11	39.99	5.56	4.16
Beech	26.69	21.90	21.66	33.75	51.65	44.35	45.80	39.45	5.21	3.86
Aspen	25.47	21.33	27.03	32.31	47.44	46.36	40.54	39.45	5.10	4.36
Oak.	34.68	27.73	17.17	27.03	48.15	45.24	44.45	42.04	4.08	3.44
Fir	34.30	24.24	18.78	29.41	46.92	46.35	40.99	40.11	2.30	1.78
Larch	26.74	26.06	21.65	32.17	51.61	43.77	42.31	38.19	2.69	2.06

These results explain themselves, if it be borne in mind that, in bringing wood quickly to a high temperature, the carbonic acid formed, and the water vaporised, react in contact with the red-hot charcoal, the first yielding carbonic oxide by absorption of an amount of carbon equal to that which it already contains, the second yielding carbonic oxide and hydrocarbons by combination (1) of its oxygen with carbon, (2) of its hydrogen, likewise, with carbon. For the same reason, air-dried wood is preferred to wood freshly felled, or to wood transported by river floating. Such woods contain a considerable amount of water capable of reducing the yield of charcoal. The amount of carbon thus transformed depends also on the temperature of the carbonisation, as first demonstrated by Pettenkoffer's experiments, and confirmed by the following results obtained by Violette:—

TABLE VI.—SHOWING THE EFFECT ON THE CARBON CONTENT OF THE CHARCOAL OF CARBONISING WOOD (PREVIOUSLY DRIED AT 150° C.) AT DIFFERENT TEMPERATURES (VIOLETTE)

Temperature to which Wood was brought.		Residuum or Charcoal obtained.	Carbon per cent. in Residuum.	Temperature to which Wood was brought.		Residuum or Charcoal obtained.	Carbon per cent. in Residuum.
°C.	°F.			°C.	°F.		
150	302	100.00	47.50	290	554	34.10	72.50
160	320	98.00	47.60	300	572	33.60	73.23
170	338	94.60	47.77	310	590	32.90	73.63
180	356	88.60	48.93	320	608	32.25	73.57
190	374	82.00	50.60	330	626	31.75	73.55
200	392	77.10	51.80	340	644	31.50	75.20
210	410	73.15	53.37	350	662	29.65	76.64
220	428	67.50	54.57	432	809.6	18.90	81.97
230	446	55.40	57.14	1023	1873.4	18.75	83.29
240	464	50.80	61.30	1110	2030	18.40	88.14
250	482	49.60	65.88	1250	2282	17.95	89.10
260	500	40.25	67.80	1300	2372	17.45	90.70
270	518	37.15	70.45	1500	2732	17.31	94.56
280	536	36.15	71.64				

L. F. Hawley and R. C. Palmer<sup>1</sup> have made laboratory tests of the relative yields of distillation products obtained in an iron tube surrounded by an oil bath and heated by burners, the maximum temperatures being 327° to 415° C., the average results being as follows:—

TABLE VII.—HAWLEY AND PALMER'S RESULTS

Species.	Weight of a Cord of Air-dried Wood. Lb.	On Dry Wood.		On a Cord of Air-dried Wood (15 per cent. Moisture).	
		Wood Alcohol, 100 per cent.	Acetic Acid, 100 per cent.	Wood Alcohol, 82 per cent. Galls.	Calcium Acetate, 80 per cent. Lb.
Beech . .	3785	1.87	5.55	11.4	299
Birch . .	3600	1.50	6.50	8.6	334
Maple . .	3875	1.93	4.95	11.7	275
Red gum . .	3330	1.75	5.16	9.3	245
Chestnut . .	2520	0.88	5.32	3.6	193
Hickory . .	4590	2.08	4.61	15.3	304
Oak . .	4320	1.385	4.70	9.2	291

Thos. W. Pritchard<sup>2</sup> describes an experimental plant for the distillation of "light" wood in which heated oil is circulated in a jacket surrounding the retort. The retort is capable of taking

<sup>1</sup> *Eighth Int. Cong. Appl. Chem.*, 1912, Section 6, p. 138.

<sup>2</sup> *Jour. Soc. Chem. Ind.*, 1912, p. 418.

a charge of 20 lb. of wood. Calculated on the results obtained with this plant the yield per cord (about 4000 lb.) of rich wood of products amount to 36 galls. of turpentine, 10 galls. of light oil, and 125 galls. of heavy oils, yielding the following refined products:—

TABLE VIII.—PRITCHARD'S RESULTS

W. w. turpentine . . . . .	40 galls.
Seconds turpentine . . . . .	1.5 "
Light oil . . . . .	10.5 "
Light product (from heavy oil) . . . . .	3.1 "
Light product (from extra heavy oil) . . . . .	2.7 "
Heavy oil . . . . .	87.5 "
Extra heavy oil . . . . .	40.6 "
Charcoal . . . . .	950 lb.
Residue . . . . .	138 "

An interesting series of experiments on the destructive distillation of some Philippine Island woods is recorded by A. H. Wells,<sup>1</sup> the retort used being of iron, heated electrically, the heat being capable of control over a range of 500° C. The results of the tests are given below:—

TABLE IX.—RESULTS OF THE DISTILLATION OF PHILIPPINE ISLAND WOODS

Botanical Name.	Wood.		Pyroligneous Distillate.	Tar.	Non-condensable Gases. <sup>2</sup>	Charcoal.	Methyl Alcohol.	Acid (as 100 per cent. acetic).
	Commercial Name.	Hardness.						
Rhizophora sp.	Baccaun .	Very hard	39.5	4.1	21.2	35.2	2.12	5.16
Bruguiera parviflora	Langarai .	"	40.8	4.2	22.9	32.1	1.84	4.95
Avicenna officinalis	Api-api .	"	43.4	5.2	19.0	32.4	1.71	4.66
Intsia bijuga . .	Ipil .	Hard	32.4	6.8	19.1	41.7	1.61	4.40
Hopea sp. . .	Yacal .	"	34.6	6.6	20.3	38.5	0.93	4.61
Shorea guiso . .	Guijo .	"	35.5	6.2	20.0	38.3	1.55	4.70
Dipterocarpus sp.	Apitong .	Medium hard	39.7	12.6	15.1	32.6	0.91	3.80
Shorea polysperma.	Tunguli .	"	39.8	7.5	18.8	33.9	1.23	2.92
Pterocarpus sp.	Narra .	"	39.4	7.8	16.0	36.8	1.36	4.37
Pentacme contorta.	White lauan	Soft	36.6	6.8	23.4	33.2	1.20	2.90
Anisoptera thurifera	Palosapis .	"	39.9	3.8	19.7	36.6	0.74	3.83
Pinus insularis .	Benguet pine	"	38.9	10.3	15.1	35.7	0.82	2.12

It was found that careful regulation of the temperature resulted in higher yields of methyl alcohol and generally in acetic acid also, confirming the observations of R. C. Palmer.

It is evident, therefore, that the woods most suitable for carbonisation, for the production of the highest yield of acetic acid and at the same time a good charcoal, are hard woods, such as oak, beech, and hornbeam. They should not be felled before they are about twenty years old, and they should be felled preferably in winter, so that the wood may not be full of sap.

<sup>1</sup> *Philippine J. Sci.*, 1917, A., p. 111.<sup>2</sup> By difference.

*Products of the Destructive Distillation of Wood:* (1) *Gaseous*.—Carbonic oxide and carbonic acid. Marsh gas and other hydrocarbons. (2) *Liquid* methyl alcohol, allyl and amylic alcohols, ether, acetone, formaldehyde, methylal, acetic, propionic, butyric, crotonic and valeric acids, and, finally, nitrogenous compounds of an ammoniacal type, amines and pyridine. (3) *Tars*.—Consisting of hydrocarbons (benzenes and paraffins), then once more methylic alcohol and acetic acid, higher fatty acids, monophenols and diphenols, a little pyrogallol, dimethylic ether and homopyrogallol. (4) *Residuum*.—Wood charcoal.

*Properties of the Principal Products of the Distillation of Wood:* (1) *Wood Charcoal*.—Good charcoal shows the grain of the wood from which it was produced; it is black and sonorous (that is, it emits a clinking sound when struck), it is not easily crushed, and does not soil the fingers. It floats on water in virtue of its porosity. It is a bad conductor of heat and electricity. Wood charcoal burns without flame; it burns more readily the lower the temperature at which it has been produced. Thus charcoal made at 350° C. (662° F.) takes fire almost suddenly, whilst that made towards 1500° C. (2732° F.) is only kindled with some difficulty. Wood charcoal has a density which varies somewhat with its origin. On an average, the hectolitre weighs 14 to 18 kilogrammes (11 to 14½ lb. per bushel) in the case of charcoal from soft woods; 22 to 28 kilogrammes (17½ to 22 lb. per bushel) in the case of charcoal from hard woods; and 30 to 35 kilogrammes (22 to 28 lb. per bushel) in the case of oak charcoal.

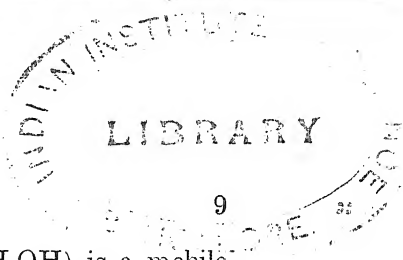
TABLE X.—SHOWING THE COMPOSITION OF THE THREE TYPES OF WOOD CHARCOAL

Kind of Wood.	C	H	O	N
Soft wood . . . . .	85.18	2.88	3.44	2.46
Hard wood . . . . .	87.43	3.26	0.54	1.56
Oak . . . . .	88.20	2.80	7.40	1.60

The calorific value of wood charcoal is generally comprised between 6500 and 7000 calories. By carbonisation in closed vessels the density of the wood charcoal obtained is low, and its calorific value is less than that obtained by forest carbonisation.

The calorific values of the charcoal from different woods are given by J. Klason, G. V. Heidenstam and E. Norlin as follows: Fir 7685, pine 7695, birch 7680, and beech 7655 calories, while the gas which is given off during the distillation has about 3.8 per cent. of the calorific value of the original wood.<sup>1</sup>

<sup>1</sup> *Chem. Zentr.*, 1909, 1, 109-110.



## INTRODUCTION.

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(2) *Methyl Alcohol*.—Methyl alcohol ( $\text{CH}_3\text{OH}$ ) is a mobile liquid with a decided spirituous odour; it boils at  $66^\circ \text{C}$ . ( $150.8^\circ \text{F}$ .); its density is 0.814 at zero. It mixes with water in all proportions. The density at  $15.5^\circ \text{C}$ . of methylic alcohol diluted with water has been determined by Dittmar and Fawsitt.

TABLE XI.—DENSITY OF MIXTURES OF PURE METHYLIC ALCOHOL (WOOD-SPIRIT) AND WATER (DITTMAR AND FAWSITT)

Per cent. by weight.	Density at $0^\circ \text{C}$ . ( $32^\circ \text{F}$ .).	Density at $15.56^\circ \text{C}$ . ( $60^\circ \text{F}$ .).	Per cent. by weight.	Density at $0^\circ \text{C}$ . ( $32^\circ \text{F}$ .).	Density at $15.56^\circ \text{C}$ . ( $60^\circ \text{F}$ .).
1	0.99806	0.99729	63	0.90276	0.89133
2	0.99631	0.99554	64	0.90056	0.88905
4	0.99299	0.99214	65	0.89835	0.88676
6	0.98990	0.98893	66	0.89611	0.88443
8	0.98701	0.98569	67	0.89384	0.88208
10	0.98429	0.98262	68	0.89145	0.87970
12	0.98171	0.97962	69	0.88922	0.87714
14	0.97926	0.97668	70	0.88687	0.87487
16	0.97689	0.97379	71	0.88470	0.87262
18	0.97459	0.97089	72	0.88237	0.87021
20	0.97233	0.96808	73	0.88003	0.86779
22	0.97007	0.96524	74	0.87767	0.86535
24	0.96780	0.96238	75	0.87530	0.86290
26	0.96549	0.95949	76	0.87290	0.86042
28	0.96310	0.95655	77	0.87049	0.85793
30	0.96057	0.95355	78	0.86806	0.85542
32	0.95783	0.95053	79	0.86561	0.85290
34	0.95500	0.94732	80	0.86314	0.85035
36	0.95204	0.94399	81	0.86066	0.84779
38	0.94895	0.94055	82	0.85816	0.84521
40	0.94571	0.93697	83	0.85564	0.84262
42	0.94239	0.93335	84	0.85310	0.84001
44	0.93911	0.92975	85	0.85055	0.83738
46	0.93575	0.92610	86	0.84798	0.83473
48	0.93229	0.92237	87	0.84539	0.83207
50	0.92873	0.91855	88	0.84278	0.82938
51	0.92691	0.91661	89	0.84015	0.82668
52	0.92507	0.91465	90	0.83751	0.82396
53	0.92320	0.91267	91	0.83485	0.82123
54	0.92130	0.91066	92	0.83218	0.81849
55	0.91938	0.90863	93	0.82948	0.81572
56	0.91742	0.90657	94	0.82677	0.81293
57	0.91544	0.90450	95	0.82404	0.81013
58	0.91343	0.90239	96	0.82129	0.80731
59	0.91139	0.90026	97	0.81853	0.80448
60	0.90917	0.89798	98	0.81576	0.80164
61	0.90706	0.89580	99	0.81295	0.79876
62	0.90492	0.89358	100	0.81015	0.79589

Methylic alcohol is separated from its aqueous solution by saturating it with dry carbonate of potash. It burns with a pale, scarcely luminous flame, and oxidises in presence of platinum black, with production of formic aldehyde. Finally, methylic

alcohol exercises a peculiar physiological action on the organism, which renders its use in food or drink very dangerous. A stère of wood yields on distillation 2 to 3 litres of alcohol. [For American yield of alcohol per cord, see Table III., page 4.]

(3) *Creosote*.—Creosote is not a well-defined product; it consists of phenol, accompanied by several of its higher homologues: cresyl hydrate or cresylol, and, according to Berthelot, of phlorol, cresol, and especially guaiacol. Creosote is a colourless, oleaginous liquid, which becomes yellowish by exposure to light; its density is 1.037 at 20° C. (68° F.); it boils at 203° C. (397.4° F.). Slightly soluble in water, creosote dissolves readily in alcohol, ether, fixed and essential oils, acetic acid and alkaline lyes. Heated with caustic soda and manganese dioxide, it forms a product which, taken up with water, yields rosolate of soda, from which sulphuric acid precipitates rosolic acid, a colour much used in yellow dyeing or calico printing.

(4) *Acetic Acid*.—Acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ) is a colourless liquid with a density of 1.064. It crystallises below 17° C., and boils at 120° C. (248° F.). Its odour is suffocating, but, after dilution with water, it is rather pleasant. Applied to the skin, acetic acid destroys the epidermis and produces vesication. It attracts moisture from the air, and mixes in all proportions with water, and with alcohol mixed with water; by dilution this acid first increases in density, diminishing afterwards, when the proportion of water is increased. The maximum density of dilute acetic acid is 1.073. It then corresponds to a mixture of 77.2 of pure acid and 22.8 per cent. of water, which would appear to be a definite hydrate expressed by the formula  $\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O}$ . The vapour of acetic acid is inflammable and burns with a blue flame; the glacial acid has the negative property of not decomposing carbonate of lime. It must be diluted with water before it reacts on that substance; a mixture of alcohol and acetic acid does not redden litmus and does not attack certain carbonates (Pelouze).

(5) *Acetone* ( $\text{C}_3\text{H}_6\text{O}$ ).—Acetone is a colourless inflammable liquid burning with a luminous flame; it is volatile, its odour is ethereal, its taste burning; its density is 0.792 at 18° C. (64.4° F.) and 0.814 at 0° C. (32° F.). Its boiling-point is 56° C. (132.8° F.). Acetone does not solidify at 15° C. (59° F.). Soluble in all proportions in water, alcohol, and ether, acetone neither dissolves calcium chloride nor potassium chloride, but it dissolves the greater number of the resins, oils and fats, camphors, etc. Gun cotton is easily soluble therein. Acetone forms, with alkaline bisulphites, crystallisable compounds, insoluble in an excess of bisulphite as well as in ether, but soluble in boiling alcohol, from which they crystallise on cooling. These compounds are likewise soluble in water and easily decomposed on boiling with

an alkaline carbonate or an acid. Under many circumstances it is thus possible to isolate acetone or to purify it by causing it to enter into this state of combination. As concentrated a solution of bisulphite as possible must be used, the reaction then taking place rapidly with disengagement of heat.

TABLE XII., APPENDED TO CHAPTER I.—SPECIFIC GRAVITY, ASH, AND WEIGHT PER CUBIC FOOT AND PER CORD OF DIFFERENT KINDS OF WOOD <sup>1</sup>

	Density.	Ash.	Lb. per Cubic Foot.	Lb. per Cord.
Ash. . . .	0.625-0.7184	0.26-0.78	38.9-46.8	2790-3350
Oak . . . .	0.6540-0.9501	0.26-1.49	40.7-59.2	2920-4220
Chestnut . . . .	0.4504	0.18	28.0	2010
Beech . . . .	0.6883	0.51	42.9	3070
Birch . . . .	0.5760-0.6533	0.25-0.31	35.9-40.8	2570-2920
Poplar . . . .	0.3889	0.96	24.2	1740
Elm . . . .	0.6506	0.80	40.5	1910
Longleaf Pine . . . .	0.6999	0.25	43.6	3120
Norway Pine . . . .	0.4854	0.27	30.2	2160
White Pine . . . .	0.3854	0.19	24.0	1720
Spruce . . . .	0.4051-0.4584	0.27-0.32	25.2-28.6	1810-2050
Hemlock . . . .	0.4239	0.46	26.4	1890
Douglas Fir . . . .	0.5157	0.08	32.1	2300
Larch . . . .	0.6236	0.33	38.8	2780
Maple . . . .	0.5269-0.6912	0.33-0.54	32.8-43.1	2300-3090

<sup>1</sup> Sharple's Tenth Report U.S.A. Census.



## CHAPTER II

### PRINCIPAL METHODS OF CARBONISING OR DISTILLING WOOD

THE different systems of carbonising wood may be grouped under one of the two following heads: carbonisation (1) by partial combustion; (2) without access of air. The first category includes the methods used in the forest, simply to convert the wood into charcoal; such charcoal being recognised as more valuable than that produced by one of the processes of the second category, where it is rather a by-product, unless it be quite a special product, such as charcoal for gunpowder.

*Carbonisation by Partial Combustion.*—These processes may be sub-divided into two sections: (1) carbonising in stacks or the forest process; (2) carbonising in ovens for the production of tar.

(1) *Carbonising in Stacks or the Forest Process.*—Generally, to reduce freight charges, wood is "coaled" in the forest where it is felled. As the wood must, above all, be protected from the action of the air, stacks are constructed in which the carbonisation is produced at the expense of the wood to be carbonised. On a dry soil, protected from the wind, a suitable site is prepared called the *foulde*. The soil chosen should neither be light nor sandy. Neither should it be compact, so that it may readily absorb the liquids which condense during carbonisation. When possible, a *foulde* which has already done duty is again utilised; the yield of charcoal is then better, and may amount to 20 per cent. The floor ought to slope from the centre to the circumference with a circular drain, so that carbonisation may be more easily effected. Only one and the same variety of timber should be carbonised in the same stack. The stack is built thus: Around some billets of wood, placed vertically in the centre of the *foulde*, chumps of wood 10 inches long are arranged so as to stand upright in layers, packing them as tightly as possible the one against the other. The diameter of each layer—separated by a few pieces of wood lying flat—gradually decreasing, imparts to the stack the form of a hemisphere or a paraboloid, the height of which is 10 to 13 feet. When the stack is finished it is covered by a layer of small plants, moss, or leaves,

then with a layer of earth or turf, leaving apertures or vents in the lower part. Then the upright billets are removed from the centre, which thereby leaves a vacant space, forming a central chimney, communicating with the vents in the lower part of the stack. The chimney is then filled with small pieces of burning wood, which set fire to the mass, and, when combustion is sufficiently far advanced, the chimney, which up to now has been well fed with fuel, is closed up; then, commencing from the top, the vents are opened so as to allow the products of combustion to escape. The smoke which first escapes is black, but it soon becomes transparent; when it is bright blue, which shows that the carbonisation is in the vicinity of the vents, the latter are stopped up, and others are opened, 10 or 12 inches lower down, and so on. When the bottom is reached all the apertures are closed, and the stack is covered with a layer of moist earth. It is now allowed to cool for several days; the earth is then removed and the charcoal produced is separated from the imperfectly carbonised proportions which are termed *fumerons*. Oak and beech thus yield 72 to 75 per cent. by volume (21 to 23 per cent. by weight) of wood charcoal. Hornbeam yields 55 to 60 by volume, and 21 per cent. by weight. For the carbonisation of resinous wood in Sweden and in Austria the stacks, instead of being vertical, are horizontal. They have the advantage of carbonising a large quantity of wood, whilst entailing less labour. The carbonisation is, moreover, more easily managed, and the charcoal obtained more uniform in quality.

(2) *Carbonisation in Ovens or Kilns for the Production of Tar.*—The use of ovens, generally, entails building expenses, and afterwards involves the transport, always costly, of the raw materials, chiefly wood.

*Rectangular Ovens.*—The use of these ovens is a transition between the stack process and that of ovens properly so called. They are built to remain stationary and consist of a rectangular brick kiln which may be closed hermetically. Vents to regulate the progress of the operation are placed at the four corners of the rectangular kiln. From 200 to 250 stères of wood are piled in this chamber, making flues at the same time which lead to the vents. The fire is brought to the centre of the oven, through a hearth situated in its axis, and carbonisation goes on, from within outwards, by means of the hot gases. The tar and pyroligneous acid collect at the bottom of the apparatus. It has also been attempted to make circular ovens on the same principle, but they have been abandoned, because they yielded wood charcoal of a quality inferior to that produced by the stack process.

*Chabeaussière's Oven.*—The object of this oven was to collect

the by-products of wood distillation in addition to wood charcoal. Carbonisation is effected in pits built of masonry, 10 feet deep, 10 feet wide at the bottom, and about  $11\frac{1}{2}$  feet at the top. These pits are closed by a dome-shaped, wrought-iron lid, pierced, first of all, by a central hole for lighting the wood, then by four other holes used to watch the extinction of the charcoal. Vents bring the air necessary for the combustion, and serve also for regulating the draught. The billets are piled horizontally in the oven, care being taken to leave a chimney in the centre. The wood is then lit, and all the apertures in the lid are stopped and the lid itself covered by a layer of earth. The distillation lasts four days.

*Schwartz Oven.*—The principle of these ovens is based on the

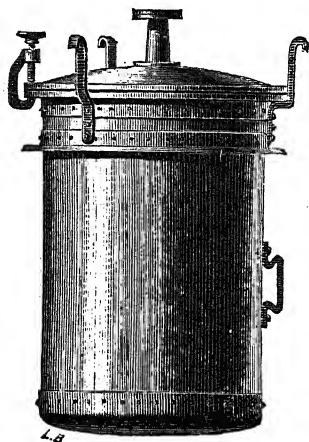


Fig. 1.—Portable vertical retort for wood distillation.

fact that a flame which does not contain free oxygen cannot burn wood, although it can decompose it. In this class of oven the carbonisation chamber has the shape of an elongated rectangle covered by an arch; on each of the two long sides of the oven the flues from an outside fireplace convey a flame without oxygen, which brings the wood to a temperature sufficiently high to carbonise it. The gaseous products escape by conduits in the middle of the small sides of the oven, and the liquids, which condense in the bottom, are collected by syphons which lead them into receivers in the vicinity.

*Chinese Ovens.*—In China the ovens are underground, and the chimney ends in the bottom of the oven; another opening on the ground level serves to regulate the entrance of air into the newly lit oven, so as to produce slow combustion, which is regulated according to the colour of the smoke escaping by the chimney.

*Carbonisation in Closed Vessels: Portable Retorts; Fixed Retorts; Continuous Retorts.* (1) *Portable Retorts.*—One of the oldest of these, but still in use in France, consists of a well-riveted, vertical, cylindrical, wrought-iron boiler, 10 to 14 mm. thick (*i.e.* from  $\frac{3}{8}$  to rather over  $\frac{1}{2}$  inch), 2 to 2.3 metres deep (from  $6\frac{1}{2}$  to  $7\frac{1}{2}$  feet), and 1.5 metres in diameter (5 feet). It is closed at the top by a lid luted with clay, and fixed by iron clamps or by screw bolts, Fig. 1. The lid has a central pipe, for the removal of the gases, etc. To the top part of the retort, underneath the circular flange, on which the lid rests, there are fixed

three iron lugs by which it can easily be attached to a crane, so as to be readily deposited in, or lifted out of, the furnace. An iron handle, fixed a little less than half-way up, facilitates the tilting of the retort, when, after distillation, it is desired to empty out the charcoal which it contains. Finally, the retort rests on the iron crown of the furnace on a strong flange, riveted to the cylinder, about 40 centimetres (say  $15\frac{1}{2}$  inches) lower than the top flange of the retort. The life of these retorts is from five to six years for the bottoms, and ten to twelve years for the cylindrical bodies. These cylinders are arranged in series of 10, 16, and even 24, in two rows, in the same mass of masonry, built so that the flames from each side do not play directly on the iron, which might otherwise become overheated. The bottoms of the retorts are, therefore, protected by fireclay bridges. The furnace gases circulate round the cylinders through flues made in the masonry arch so as to escape to the chimney, by an upper orifice placed directly underneath the iron crown of the furnace. A furnace consumes 200 kilogrammes of coal (about 4 cwt.) in winter, and 150 kilogrammes (about 3 cwt.) in summer per twenty-four hours in carbonising 10 stères of wood, or on an average 15 to 20 kilogrammes per stère (cubic metre), *i.e.* 33 to 44 lb. of coal. When the size of the installation admits of it, the retorts are sometimes heated by gas generators adjacent to the bench of retorts, so as to avoid the loss of heat inevitable with long conduits. The handling of the retorts is performed by the aid of a travelling bridge, carrying an elevating apparatus or hoisting tackle both worked either by hand or electrically as shown in Fig. 2. The retort, when distillation is complete, is withdrawn from the furnace, and transported outside, to be emptied of the charcoal which it contains, whilst another retort, charged with wood, is put in its place, so that the work suffers no interruption. When the retort containing the charcoal is sufficiently cool, it is opened, then it is placed on a bascule to empty it of charcoal. In certain factories, in order to diminish the number of retorts and consequently the initial installation capital, the cylinder is opened as soon as it comes out of the furnace house, and its glowing contents are tilted into wrought-iron extinguishers. Advantage is then taken of the retort being in a horizontal position to charge it with fresh wood. Sometimes an iron crate is used to receive the retort from the crane, so as to facilitate emptying; these crates have two diametrically opposite pivots upon which they can turn. An adjustment fixes the retorts in the crates. In some installations a single hearth does duty for two carbonisation furnaces. By means of dampers for the furnace gases, and of small fans for the permanent gases, these gases are directed into one or other of the furnaces, so as to bring the retort, which is nearing

the end of its distillation, to a higher temperature. By this arrangement a constant fire can be kept on the grate, a considerable saving in fuel being realised; at the same time there is greater regularity in working, which does away with the *fumerons* (partly burnt pieces) in the charcoal.

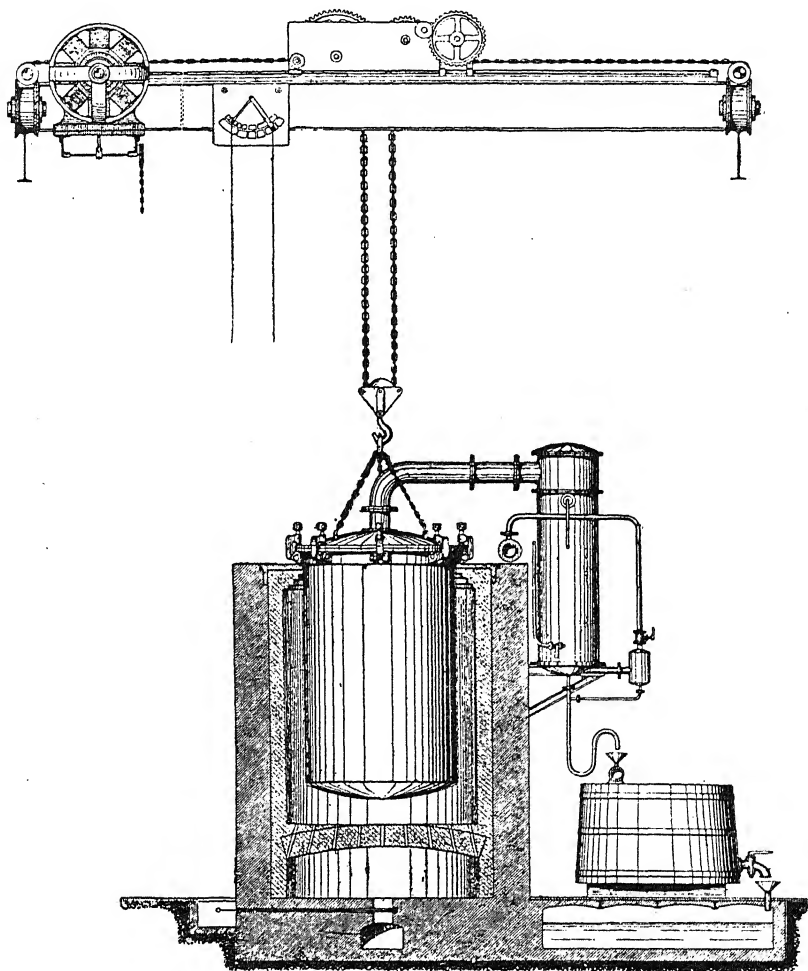


FIG. 2.—Portable vertical retort for wood distillation with hoisting and lowering tackle.

(2) *Fixed Retorts—Vertical and Horizontal—and Large-sized Continuous Retorts. A. Cylindrical Vertical Retorts.*—This type, being almost obsolete, is only described as of interest historically. Mollerat frères were, in 1810, in France, the first

to invent this type of plant for extracting pyroligneous acid from wood heated in closed vessels. Their apparatus consisted of a large wrought-iron cylinder of 3 cubic metres capacity, built into a brick furnace, heated by a fireplace under the retort, and so constructed that the combustion gases circulated round the cylinder before passing to the chimney. A manhole was inserted in the lid for charging the cylinder and for the discharge of the charcoal formed by the carbonisation of the wood, when the operation was terminated. A pipe in the side of the upper part of the retort led the distillate to a condenser. Kestner afterwards modified this plant by closing the cylinder by a removable lid held by iron clasps, and inserting an orifice in the

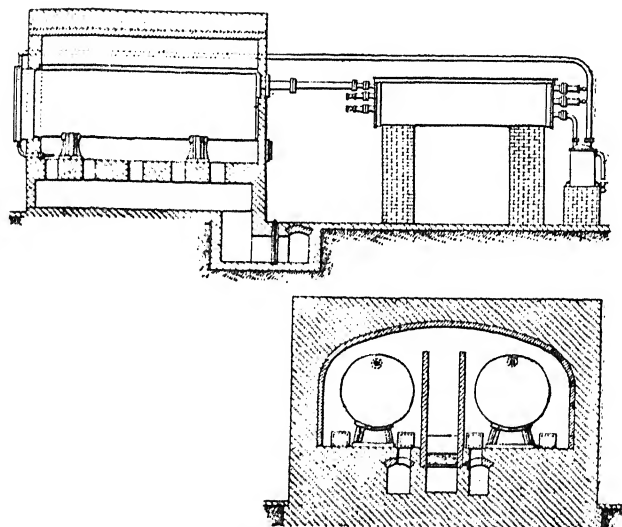


FIG. 3.—Cross section and longitudinal section of furnace or oven with two horizontal retorts for wood distillation and arrangement for utilising the gas produced for heating the retorts.

bottom for the discharge of the charcoal, which was then collected in cast-iron extinguishers. This system entails a much larger plant to work the same quantity of wood than an installation with portable retorts.

*B. Horizontal Cylindrical Retorts.*—In Great Britain, in Sweden, and in Germany, wood is distilled in cylinders laid horizontally in the furnace and heated from the one fireplace (Fig. 3). The two ends are closed either by clay-luted, cast-iron doors or by cast-iron doors with two handles, and kept in position by a system of iron crosspieces, carrying a tightening screw like gas retorts. One end of the cylinder has in its closing disc, which is not dismantled except for repairs, a pipe for the

removal of the distillation products. As to the other door, it may be used for charging the wood into the retort, and then for discharging the charcoal, which is run into wrought-iron extinguishers. These cylinders hold a charge of 5 stères of wood, the distillation of which requires eight hours. This type of retort has lately undergone many modifications. The retort has now only one door, as shown in Fig. 4, placed in the smoke-box of the furnace. This plan gives better results in the carbonisation of the wood, as all parts of the retort are heated. A charge of up to 5 stères of wood requires sixteen to twenty-four hours for complete carbonisation.

C. *Large-sized Furnaces.*—In certain German districts large horizontal retorts are used, capable of taking a charge of 30 to 50 stères of wood. They are heated, not only on the exterior,

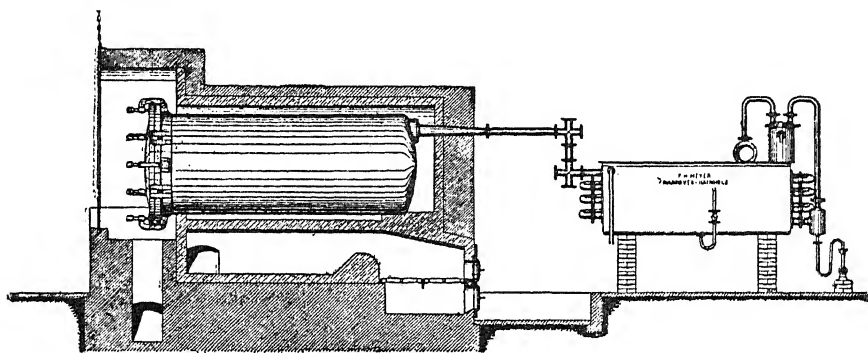


FIG. 4.—Furnace for wood distillation with two horizontal retorts with only one door for closing.

but also on the interior by two wrought-iron chimneys starting from the bottom of the retort. A charge in this type of retort takes four to six days (Fig. 5).

The *Stack Furnaces*, a view of which is given in Fig. 6, are on the same plan as those used in America, in Russia, and in Hungary. They are built of masonry and—everything else being equal, even as regards products obtained—can be run, in proportion to size, cheaper than other plant. They can be charged up to 300 stères (84 cords), each charge taking twenty days. At the exit of the condensers the gases are propelled by a fan under the stacks, where they are burnt as fuel.

D. *Continuous Distillation Plant.* The *Astley Paston Price Furnace*.—This furnace, built of fireclay bricks, consists of a large chamber, the floor of which slopes slightly. It can accommodate three trucks charged with wood. It is closed at the ends by iron doors, and is divided by wrought-iron partitions separating the middle truck from the two others. The fireplace

being directly underneath the second truck, the latter is then in the hottest part of the furnace and is in full distillation whilst the first is cooling, protected from air, while the third, and last introduced, is undergoing a preliminary drying. The gases and condensable vapours escape by pipes fixed in the roof of the middle compartment.

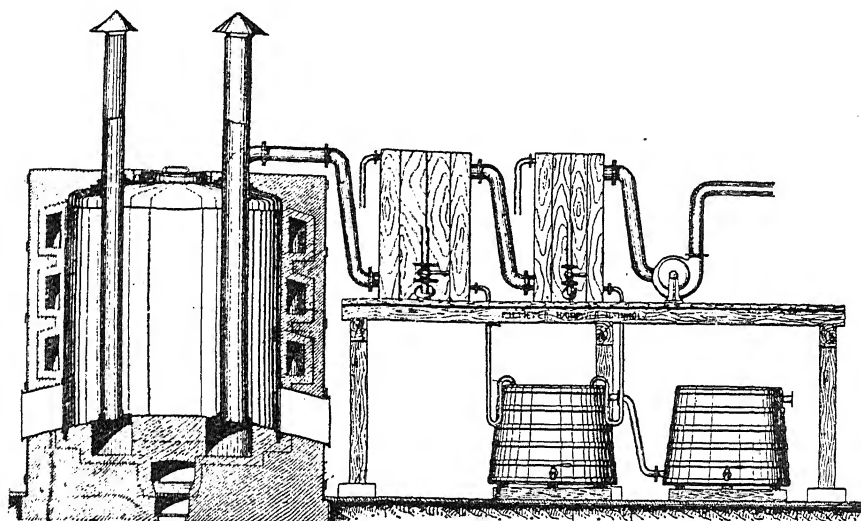


FIG. 5.—Capacious vertical retorts for wood distillation with internal and external heating arrangements.

*Bresson's Vertical Furnace* is a modification of the preceding, but it differs in the plant used and in the fact that the wood to be carbonised is moved vertically instead of horizontally. It consists of five super-imposed, jacketed, cast-iron

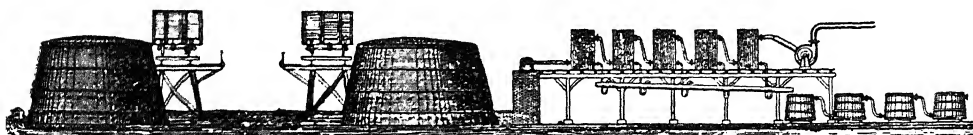


FIG. 6.—Masonry stack ovens or furnaces for wood distillation on very large scale and appropriate condensation plant.

cylinders, supported by a piston in the bottom. The three middle cylinders are in full heat in a masonry furnace whilst the lower cylinder is cooling and the wood in the uppermost one is undergoing a preliminary drying. Horizontal dampers allow the three cylinders in course of distillation to be isolated. The volatile products disengaged from the wood escape through



a pipe, which penetrates to the uppermost part of the third upper cylinder and leads to a condenser, whilst the permanent gases pass to a gasometer, from which they are conducted by the pipe back to the fireplace, where they are burnt. In this furnace wood is distilled in forty-eight hours, passing gradually from a temperature of  $250^{\circ}$  to  $700^{\circ}$  C. ( $482^{\circ}$  to  $1292^{\circ}$  F.). According to Bresson, the yields of distillation products are notably higher than those obtained with other plant, in consequence of a slower and more methodical carbonisation; moreover, the charcoal so produced is of a better quality.

*Distillation of Sawdust.*<sup>1</sup>—The distillation of this product could be carried out in ordinary retorts, but it would present some difficulties, in consequence of the moisture contained in the sawdust, etc. Moreover, a non-conducting envelope of charcoal forms at the commencement of distillation, which renders the penetration of the heat to the centre of the mass difficult, and afterwards retards the disengagement of the distilled products. Confronted with the impossibility of rationally distilling these waste products, resource has been made to the use of mechanical methods for handling the raw material. Holliday invented a plant in which the wood waste is fed in at one end of the retort through a hopper, whilst an Archimedean screw gradually conveys it to the other extremity, the material being carbonised in its passage through the apparatus; the gases and vapours disengaged are led by a special pipe to a condenser, whilst the very finely divided wood charcoal which results from this operation falls to the bottom of the retort and passes through a pipe into a vessel filled with water. This process consumes much fuel, besides which it yields a dilute distillate very costly to evaporate. To remedy these defects the Holliday process was modified by employing several cylinders fixed one above another, the bottom one receiving the main heat from the fire, whilst the top one is heated by the waste heat. The wood waste is introduced in the top part of the plant, where it is freed from the bulk of its water. It then describes a zig-zag course as it passes from one cylinder to another, to issue completely carbonised through the bottom of the lowest cylinder. In another process, retorts analogous to an acetone retort are used. Two similar retorts, one above the other, communicate by pipes. In the upper retort a preliminary drying is effected, in the second the distillation proper is conducted. Meyer's plant for the distillation of wood waste consists of two horizontal retorts, into which there are introduced, through sliding doors, trucks with a number of shelves, on which the material

<sup>1</sup> For a full treatment of this branch of wood distilling, see Hubbard's *Utilisation of Wood Waste* (Scott, Greenwood & Son).

to be distilled is spread in a thin layer. Whilst carbonisation is proceeding in the one retort, the wood waste is being dried in the second. The carbonised wood waste is withdrawn on the trucks into cooling chambers. By this method, owing to stirring being unnecessary, working expenses are lower than in the previous methods, and finally the hot retorts can be recharged immediately. Bergmann, in his patent, proposed to agglomerate wood sawdust in the form of briquettes which were carbonised in ordinary retorts, thus avoiding the drawbacks already referred to; but this process was soon abandoned, as, in order to distil these compressed materials, the retorts must be brought to a high temperature, and the plant very quickly wears out.

R. C. Palmer<sup>1</sup> has shown that in the distillation of hard-

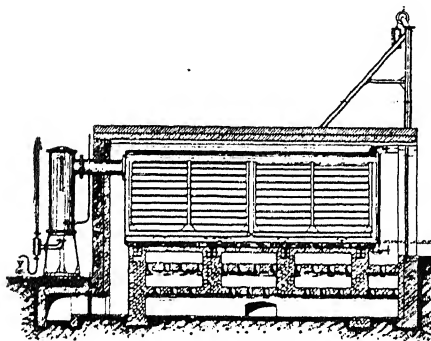


FIG. 7.—Retort for the carbonisation of smalls or wood waste.

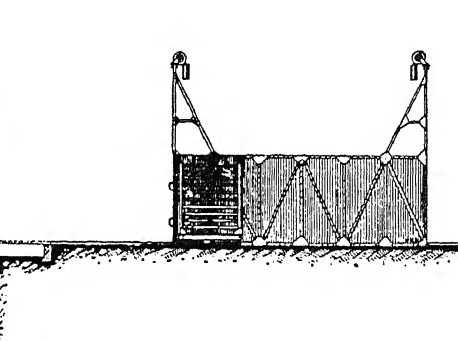


FIG. 7A.—Retort coolers for cooling the retorts (Fig. 7) after an operation.

wood the temperature control is of the utmost importance to the yield of products obtained. Thus by raising the temperature rapidly to the point at which the exothermic reaction took place and when destructive distillation actively commences, and then lowering the external heat, yields of 45 per cent. more alcohol and 40 per cent. more calcium acetate could be obtained. Thus in actual experiments with this method of operation yields of 10·66 gallons of 95 per cent. wood alcohol, 213·6 lb. of calcium acetate, and 54·8 bushels of charcoal were obtained per cord of wood, whereas by the ordinary method of heating the yields were 8·2 gallons of wood alcohol, 187 lb. of calcium acetate, and 53·5 bushels of charcoal. The wood used in these experiments was principally maple, the time required being the usual period of twenty-four hours, but rather more fuel was consumed in the firing.

<sup>1</sup> *Jour. Ind. Eng. Chem.*, 1915, p. 663.

*Working Routine: (1) Horizontal Retorts.*—The wood charcoal having been just discharged, the retort is filled with wood as dry as possible, charging the bottom first; the door is closed and the fire urged. In ten minutes the distillation commences, as may be seen by the great increase of temperature in the goose-neck; then condensable products pass over accompanied by permanent gases. The liquid, which condenses, first of all is run away because it contains the greater part of the hygroscopic water contained in the wood; it is only slightly acid, and holds in solution some traces of tarry matter. Then the strength in acid increases, and the coloration, owing to the greater amount of tar, is deeper. For retorts of 2 cubic metres capacity the distillation lasts about fourteen hours; at the end of that time the quantity of condensed products is negligible, the disengagement of gas ceases, and when the goose-neck commences to cool the operation is finished. The fire is withdrawn and the door of the cylinder is soon opened, and the wood charcoal, which then becomes incandescent, is withdrawn by means of rakes. It falls into wrought-iron receivers which are then fitted with close covers and in which it cools without access of air. The receivers are then taken away, and after making sure that the neck of the retort is not obstructed by condensed tar, a fresh charge is made with wood brought on a truck.

*(2) Vertical Retorts.*—The cylinder being filled with 4 or 5 stères of wood, taking care to utilise its capacity to the utmost, the lid is put on, and it is laid in position in the furnace; distillation commences; it is carried on open to the air until all moisture is expelled, that is to say, until the previous white smoke becomes blue. The neck of the retort is now connected with the disengagement tube, which is luted with clay. So long as the distillate does not run clear it is collected apart to be converted into brown acetate of lime; when it becomes bright brown and tests strong (*de titre fort*), which occurs in normal working at about the fifth hour, it is sent to the grey acetate reservoir direct. Ten hours after starting, when the distillate commences to brown, it must be sent to the brown acetate reservoir. If a factory using vertical retorts be compared with one using horizontal retorts, it will be remarked that there is no advantage in the first system, except in the quality of the charcoal produced, provided that this charcoal be allowed to cool a certain time in the retort, which involves a much greater number of retorts. Everything else being equal, it is recognised that vertical retorts have no advantage over horizontal ones.

*Condensation Plant. Condensers.*—As in every similar industry, the condensation of the distillate from the carbonisation of wood is very important. A badly planned installation may lead to losses, which can only be prejudicial to the manu-

facturer. In fact, the gas from the retort carries with it acetic acid, acetone, and wood-spirit, and, as wood yields about 20 per cent. of its weight of permanent gas, it follows that in the case of a factory treating 50 tons of wood a day, 8000 cubic metres of gas are produced, capable of carrying with them a large proportion of the condensable products, which are burnt in the fire. In summer, as the temperature of the water used for condensation is high, as much as 50 per cent. of methyl alcohol and acetone and 10 per cent. of the acetic acid may thus be lost. It is therefore necessary in installing a factory to construct the refrigerating condensers with a large surface development, so that, even with the strongest distillation of gas and vapours, the distilled products are brought to the temperature of cold water as they issue from the condenser. No hesitation should be made in installing complete and sometimes costly condensa-

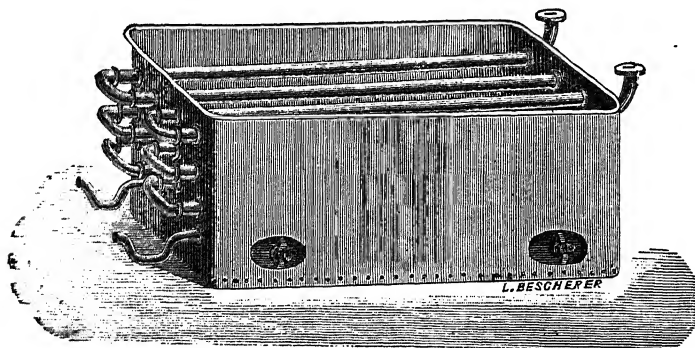


FIG. 8. —Horizontal condenser for cooling distillate.

tion plant, especially so with powerful carbonising plant. As tarry deposits are apt to form in the pipe which carries away the distilled products, which, by becoming calcined, would obstruct the pipes, it is well not to have the condensers too far removed from the retorts. In the early days of wood distillation the condenser consisted simply of four horizontal copper pipes supported on a wooden or iron frame, communicating with each other by three elbow joints, and completely enveloped by wrought-iron jackets, in which water circulated. This cold water flowed from a reservoir into the lowest jacket, close to where the condensed products issued, then passed successively into the other upper jackets by means of small vertical pipes, which connected the annular spaces between the pipes and their jackets. The condensed products flowed into a reservoir, whilst the permanent gases were led by special piping to the retort furnaces, where they produced in burning such a heat that for the time being no other

fuel was necessary. In more modern factories the condenser consists of a rectangular wrought-iron tank (Figs. 8 and 9),

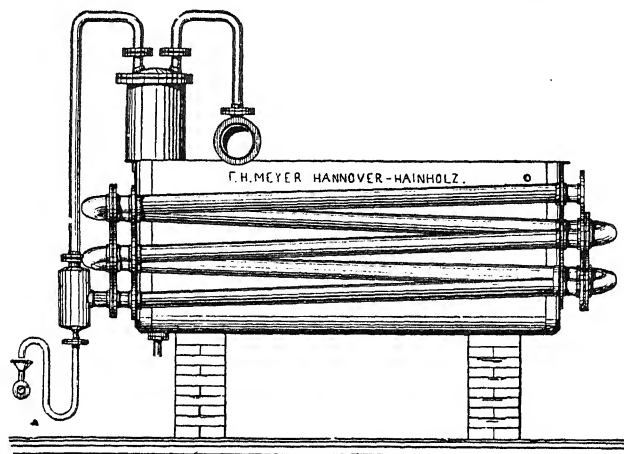


FIG. 9.—Condenser (cooler) with its separator and gas collector.

containing a series of copper tubes, slightly sloped to allow

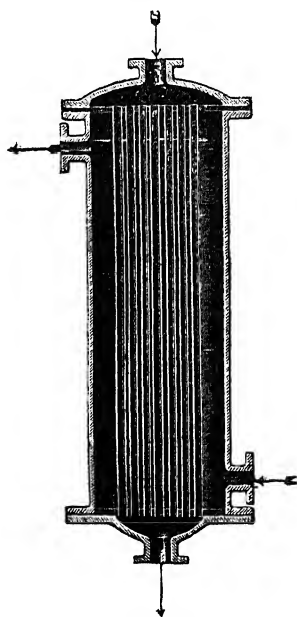


FIG. 10.—Tubular condenser (cooler), vertical.

the condensed liquid to flow out. These pipes are fixed in the tank by collars bolted on the opposite short sides. They are connected up in pairs on the outside by brazed copper sleeves and elbows. They are easily dismantled for cleaning. A current of cold water enters at the bottom of the tank and issues through an overflow pipe situated a few centimetres below the upper edge of the condenser. Meyer's tubular bundle condensers are either vertical or horizontal. With a maximum condensation they consume the minimum of water. As shown in Figs. 10 and 11, they can easily be cleaned by removing one end. As they issue from the condenser the liquid and incondensable gases pass to a separator and gas washer, thence they pass into the furnaces, as will be seen later. Fig. 12 shows a wooden condenser installed at the end of the large stack furnaces taking stères of wood, in which the gases are propelled by a fan.

In order to diminish the loss due to entrainment by the permanent gases, which always remain saturated with vapour, Vincent, by a special arrangement, which gives excellent results, utilised

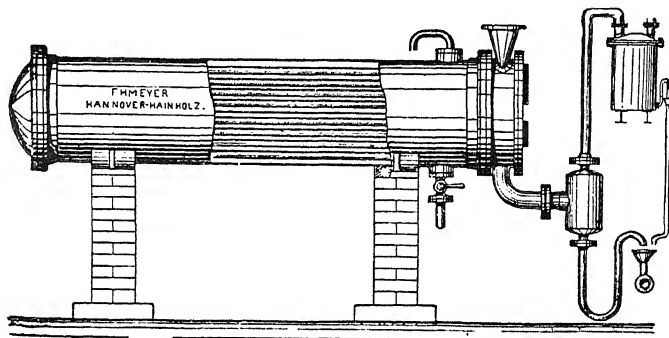


FIG. 11.—Tubular condenser (cooler), horizontal.

the cold, produced by dissolving certain salts used in the manufacture of the derivatives, carbonate of soda for instance. He passes the cold gases, as they come from the condenser, through a layer of carbonate of soda 70 to 80 cm. deep, spread on a double

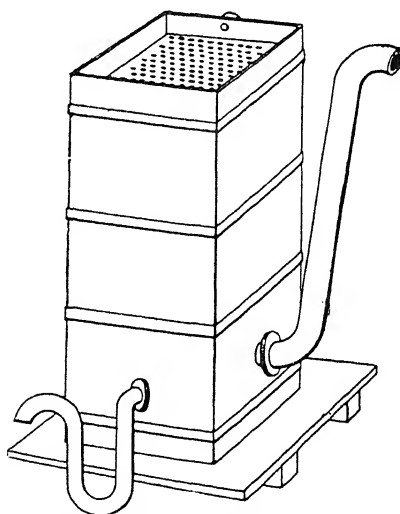


FIG. 12.—Wooden condenser for large stack ovens.

bottom in a copper column. Under the influence of the current of gas saturated with water and with acid, the crystals of carbonate of soda gradually dissolve and becomes converted into acetate of soda, producing at the same time a considerable lower-

ing of temperature, which causes an abundant condensation of utilisable vapours. The liquid, drawn off by a tap placed in the lower part of this apparatus, is afterwards distilled yielding crude methyl alcohol, which is condensed, and an alkaline residue, which is used in making acetate of soda. In more

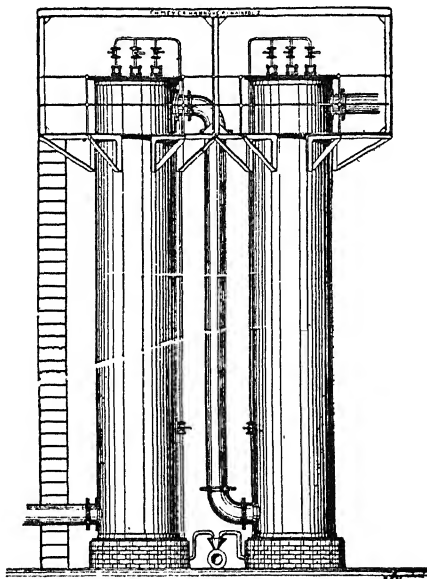


FIG. 13.—Pair of coke scrubbers for condensing gas.

recent installations the gases are passed through one or two coke towers (Fig. 13) through which water or weak pyroligneous acid trickles from above. As they issue from these towers the gases contain, according to the stage at which the distillation of wood has arrived, the following :—

TABLE XIII.—SHOWING THE COMPOSITION OF GASES FROM WOOD DISTILLATION AFTER PASSING THROUGH COKE SCRUBBERS

	In Beginning, per cent.	At End, per cent.
Carbonic acid, CO <sub>2</sub> . . . . .	44.90	29.20
Carbonic oxide, CO . . . . .	36.80	34.90
Hydrogen as hydrocarbons . . . . .	16.80	34.20
Nitrogen . . . . .	1.50	1.70
	100.00	100.00

They are then made to pass by means of a Koerting injector into a lime purifier which retains carbonic acid, whence they pass to the furnaces to be burnt.

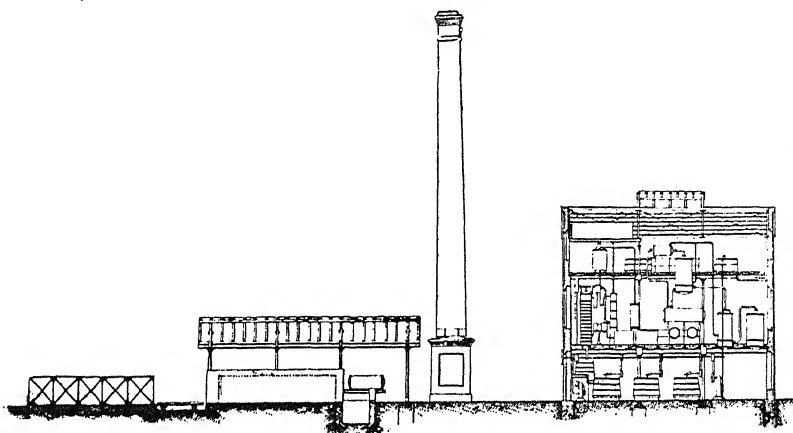
*Installation of a Wood Charcoal Factory. General Considerations.*—Many things have to be considered in choosing a site for a wood carbonisation factory. Besides raw material, such as wood, coal, and lime, which enter into this industry, the facilities for transport both by rail and water which would be at disposal must be taken into account as well as the water supply, the requirements for which are great, especially for the condensation of the products disengaged by the distillation of the wood. Since an ideal factory is difficult to realise, it is necessary to get as near as possible to the forest, the wood of which it is proposed to distil, so as to reduce freight charges on the raw material to a minimum, whilst having at the same time near-by a railway, a stream or a canal, by which lime and coal can be received and the finished products despatched. A factory (Fig. 14) situated far from a wooded district would be placed at a great disadvantage, although the floating of timber could be utilised. The floating of timber as a method of transporting wood should be entirely abandoned, because it is recognised that the best yields in distilled products are got from wood as dry as possible. It is evident, however, that this floated timber can be stacked for several months before manufacture; but, during its slow drying in the air, it undergoes decomposition, more or less profound, which renders it less combustible; consequently such wood on carbonisation yields more tar and a charcoal which, being more friable, is less valuable. The cost of the wood delivered at the factory is a most important item. This leads to the conclusion that such an industry should be installed only in districts where wood is cheap. However, this condition is not paramount, for the wood charcoal must be sold at a remunerative price, therefore labour must be cheap, as well as coal, of which a large amount is consumed. It will, therefore, be necessary to be as near as possible to the chief outlets for wood charcoal, that is to say, to be in the neighbourhood of large towns, where fuel is required, and not to be too far removed from industrial centres, which consume a large quantity. Besides, such a factory should be a little distance away from dwellings on account of the fumes given off. Likewise, as the residual waters contain a certain amount of empyreumatic products, they cannot be allowed to flow direct into running streams but must be passed through a filtration pit, which retains the oil and tars, to be subsequently collected and burnt.

*Arrangement of the Different Buildings in a Wood Carbonisation Factory.*—The steam boilers and their feed tanks ought to occupy a building in the central part of the factory,



around which the other buildings should be grouped. It is necessary to place the engine room (containing steam engine, dynamo, water pumps) as near as possible to the boilers so as

(1)



(2)

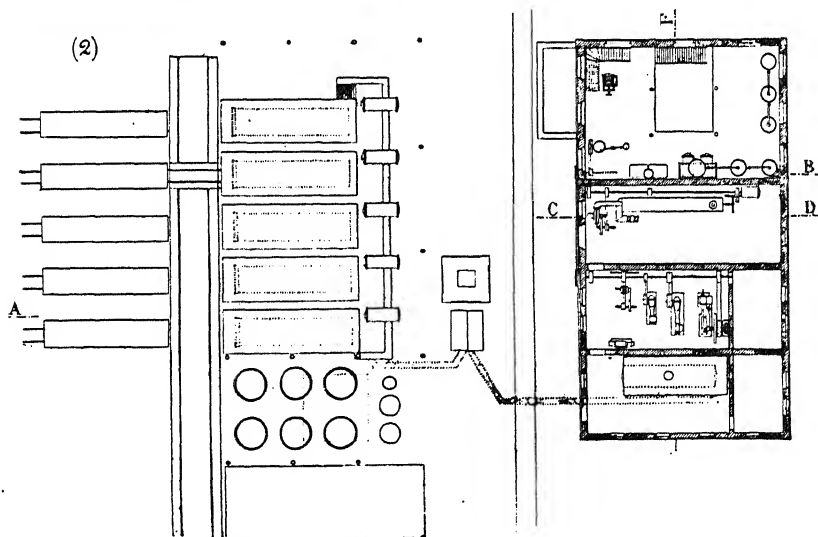
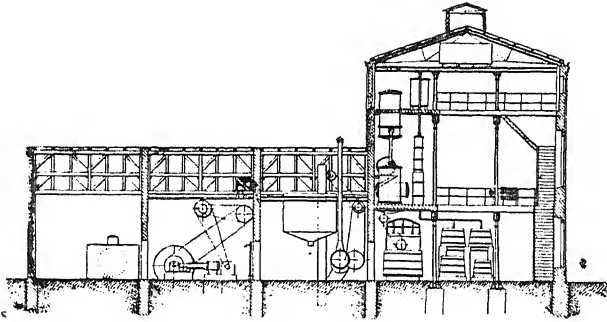


FIG. 14.—Plan, sections, and elevations of a wood distillery capable of treating 100 stères (27 cords) of wood daily. (1) Sectional elevation along AB of ground plan. (2) Ground plan.

to have the steam pipes as short as possible and thus conserve the heat for the machines requiring it. In another building, also near to the boilers and not far removed from the buildings

(1)



(2)

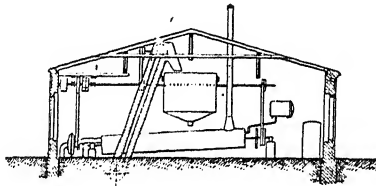


FIG. 14A.—Plan, sections, and elevations of a wood distillery capable of treating 100 stères (27 cords) of wood daily. Sectional elevation (1) along CD; (2) along EF of ground plan (Fig. 14).

where the distilled products are treated—the latter requiring a large amount of steam—are installed the monte-jus, the pumps for crude pyroligneous products, for acids and the filter presses (Figs. 15, 16, 17). For the type of boilers, steam engines, feed

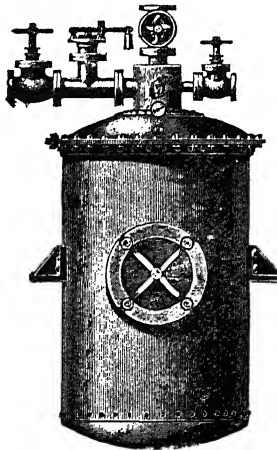


FIG. 15.—Monte-jus.

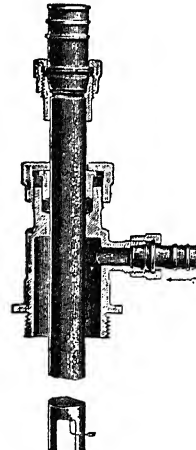


FIG. 16.—Arrangement of the plunger pipe of monte jus.

1402

6748

1221

pumps, etc., required, the reader is referred to the chapter on tannic acid extracts. The retorts are placed in front of one of the faces of the quadrilateral occupied by the factory; the part of the ground where the sheds will be installed, under which the wood is stacked during the season of inclement weather whilst waiting to be distilled, will occupy a face of the factory perpendicular to that of the retorts. The wood charcoal warehouse, as well as the space reserved for coal, is in front of the retorts. Ordinary railways for the reception of raw material and the despatch of different manufactured products traverse these different timber yards or sheds as well as the buildings. Finally, an installation of trucks on narrow tram lines will help in the handling of all sorts of materials.

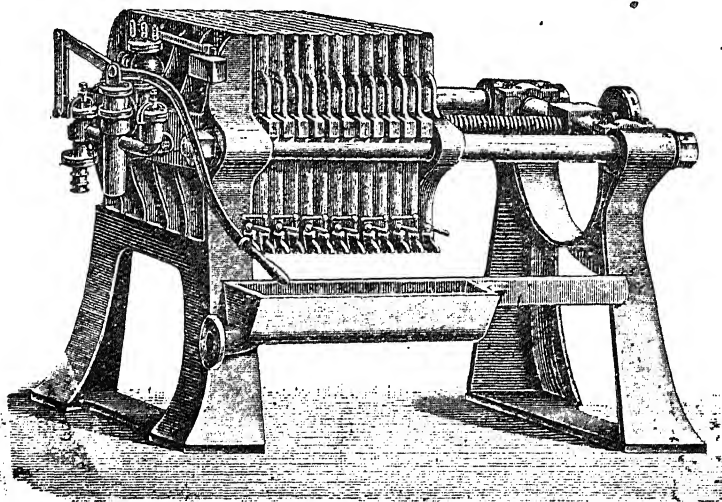


FIG. 17.—Filter press.

*Store Tanks.*—The water for feeding the boilers or for the condensers is contained in wrought-iron or reinforced concrete tanks, fixed at a certain height in the factory, for instance, above the steam engines and pumps. As the temperature and the quality of the water for the condensers plays an important rôle, it will be necessary to use well water, which must be free from any substance which can attack copper or iron. It must neither be muddy nor too calcareous, so as to avoid incrustations on the coils, which would lead to a diminished condensation. It is calculated that a factory treating up to 100 cubic metres per day requires, on an average, 10 cubic metres of water per stère for condensation (1) of the products distilled from the carbonising retorts, (2) of the products distilled on the separa-

tion of acetic acid and methyl alcohol, (3) of the products obtained by the rectification of methyl alcohol. To feed the steam boilers, it will be preferable to install a special reservoir which collects the condensed steam from the different apparatus and machines where steam condenses, such as the coils of pans and stills, or from the evaporation of acetate of lime as well as the exhaust from the steam engine, such water having the advantage, like all distilled water, of containing no mineral matter. To the tank, which supplies the condensers with water, a draw-off pipe is fixed for use in case of fire. Fire appliances are installed in every building, so as to give first aid until the main pump is set in action, which may be permanently erected in the pump room connecting its pressure with the water main. It draws the water direct from the tank, or from a stream, or canal. In the buildings where tars and oils are treated there

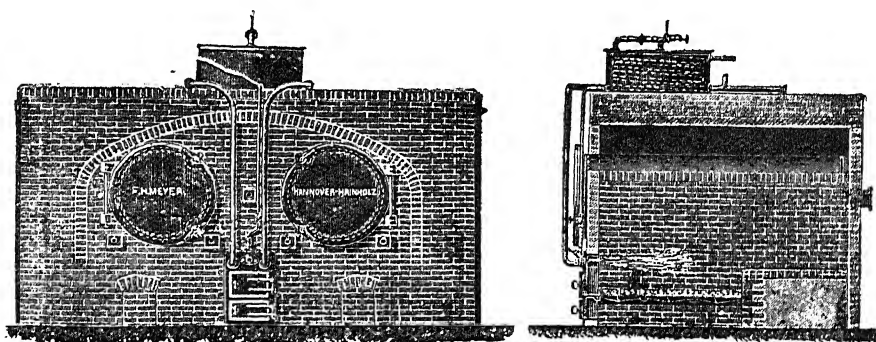


FIG. 18.—Arrangement for burning the tar under the monte-jus.

ought to be a sufficient supply of sand, to extinguish any incipient fire that may break out. To feed the different apparatus installed in the building where the products are treated, it will be preferable to have feed tanks fixed to each apparatus. These tanks, fitted with a counterpoised float, rising and falling in front of a graduated scale, are filled, when required, by pumps or monte-jus installed in the same building. Finally, tanks containing commercial products like methyl alcohol, acetone, etc., are grouped in a part of the factory far away from fire of any kind, so as to isolate them and thus prevent them being set ablaze by the first outburst of a fire. For greater security such tanks are surrounded by a brick wall.

*Use of Tar to Heat Retorts or Steam Boilers.*—The tar may serve, like the permanent gas, to heat the retorts and the steam boilers. Two kinds of tar have to be dealt with: (1) the tar which separates mechanically from the pyroligneous distillate;

In a factory treating 110 stères of wood weighing 380 kilogrammes, that is to say, 41·8 metric tons per twenty-four hours, the products obtained are approximately :—

TABLE XIV.—SHOWING RESULTS OBTAINED IN A WOOD CHARCOAL FACTORY. SOME DATA FOR ESTIMATING COST OF PRODUCTION

1. Wood charcoal: Total 12.1 tons { Large lumps, 11 tons.  
Small lumps (waste), 1.1 tons.
2. Tar, 2½ tons, which distilled gives { Water free tar, 2.2 tons.  
Pyroligneous acid, 0.550 ton.
3. Pyroligneous acid, 17.600 tons, { decomposed 1.650 tons tar, { 2.640 tons  
plus above 0.550 ton { in the three- 18.200 tons of a { of grey  
pan system { solution of ace- acetate of  
yields { tate of lime, lime 80  
{ which yields per cent.  
{ 5.500 tons of  
{ wood-spirit  
{ phlegms, which  
{ when rectified  
yields { 0.66 ton  
{ of 80 per  
{ cent. crude  
{ wood-spirit.
4. Gas, 8.550 tons used in heating the retorts.

The plant consists of fourteen movable retorts, which, by taking twenty to twenty-two charges per twenty-four hours, enables the above amount of wood to be passed through them. As each charge is carbonised, by means of the travelling crane, the hot retort is lifted out of the furnace and laid on a truck to be immediately replaced by another freshly charged and brought in proximity to the spot; the time of charging and discharging the retort does not exceed more than eight to ten minutes on an average. Fifty workmen being employed in the factory, and

labour costing 1·85 to 2·45 francs per day, the labour equals about 2·1 francs per stère of wood. This cost may vary, especially if there is a break-down or there are slack days. The lime used per stère averages 0·18 franc. As to coal consumed it is necessary to estimate on 100 to 105 kilogrammes per stère, which comes to 2 to 2·5 francs, taking the price of coal as 22 to 25 francs the ton according to the district in which the factory is situated. The general expenses of such a factory amount to 3·15 to 3·70 francs per stère of wood carbonised, in which it is necessary to include the interest on the capital employed, which may amount to as much as 750,000 francs (say £30,000), of which 400,000 francs (£15,000) are for plant, 280,000 francs (£11,200) for purchasing wood, and the remainder as working capital.

A very comprehensive paper on the distillation of wood was contributed to the Glasgow Section of the Society of Chemical Industry on November 27, 1917, by James C. Lawrence,<sup>1</sup> which is well worth studying. Among other things he mentions the distillation of woods rich in rosin, *e.g.* pitch pine, or long leaf yellow pine, Norway pine, and fir for the recovery of turpentine which is done either by superheated steam, by an oil jacket, or even by oil or rosin in the retort itself. The temperature of the retort is kept below 200° C. until the volatile products have passed over in order to contaminate the turpentine as little as possible. The temperature is then raised and the distillation products collected as usual. The tar is either shipped in its natural condition or is itself distilled and the products rectified, yielding—

Rosin spirits distilling between . . . . .	80° and 150° C.
Wood turpentine . . . . .	150° „ 180° C.
Pine oils . . . . .	175° „ 250° C.
Rosin oil . . . . .	250° „ 400° C.

The following figures show the yields obtained in the distillation of different woods:—

TABLE XV.

Products.	Four cords rich wood, weight 16,600 lb.	Four cords lean wood, weight 16,000 lb.	Four cords hard wood, weight 14,000 lb.
Charcoal . . . . .	4284 lb.	4400 lb.	3600 lb.
Refined turpentine . . . . .	41·5 galls.	20·75 galls.	—
Pine oil . . . . .	11·6 „	4·2 „	—
Rosin spirit . . . . .	21·5 „	12·0 „	—
Rosin oil . . . . .	141·0 „	64·75 „	—
Creosote oil . . . . .	46·5 „	21 „	20 galls.
Acetate of lime 80 per cent. . . . .	300 lb.	350 lb.	852 lb.
Wood alcohol (spirit) . . . . .	6 galls.	9·6 galls.	37·5 galls
Pitch . . . . .	1400 lb.	625 lb.	720 lb.

<sup>1</sup> *Jour. Soc. Chem. Ind.*, 1918, p. 5 T.

In the distillation of hardwoods, the author states that the figures given for the yield are somewhat misleading since they are often calculated on the cord or ton of wood; the cord being anything from 64 cubic feet to 256 cubic feet according to the country and district referred to, while cords of wood of 128 cubic feet may vary in weight more than 100 per cent., and still contain approximately the same weight of actual dry material. The following yields of various types of distillation plant are calculated on a ton (2240 lb.) of actual dry wood, free from moisture:—

TABLE XVI.

Plant.	Charcoal. Lb.	Acetate of Lime, 80 per cent. Lb.	Wood Alcohol. Imp. Galls.	Boiled Tar. Imp. Galls.	Coal used for Fuel. Lb.
1. British cordwood type .	795	164	4.13	12	235
2. Mechanical retort .	729	137	2.26	18	122
3. American cordwood type	815	158	5.54	11	178
4. Commercial experimental	826	162	6.56	—	—
5. Laboratory experimental	—	197	6.7	—	—

The wood alcohol includes all low-boiling ketones, esters, and aldehydes usually present in the 95 per cent. commercial product.

(1) Wood, mostly oak, in pieces 1 to 2½ inches thick and containing 30 per cent. of moisture. The acetate of lime actually tests 84 to 86 per cent.

(2) Wood, mostly birch chips, and very dry. Acid strength of crude liquor 10 to 12 per cent. The acetate of lime tests 75 to 78 per cent.

(3) Wood, mostly maple, in logs 4 to 8 inches in diameter containing about 15 per cent. of moisture.

(4) Hawley and Palmer's experimental results.

Lawrence also gives the percentage yield of products from various kinds of wood from which it will be seen that birch yields

TABLE XVII.

Species.	Charcoal. Per cent.	Acetic Acid. Per cent.	Wood Alcohol. Per cent.	Tar. Per cent.
Oak (English) . .	36.1	5.40	1.58	14.7
Oak (American) . .	35.0	5.12	1.33	6.3
Maple . . . .	36.8	4.92	2.02	12.6
Beech . . . .	38.4	5.22	1.95	9.9
Birch . . . .	39.1	6.48	1.45	10.4
Wattle (mimosa) . .	37.5	5.68	1.50	12.8
Soft pine (white wood)	38.8	2.47	1.01	20.2
Average . . . .	—	5.47	1.65	—

Selected from  
Hawley and  
Palmer's figures.

about 20 per cent. more acetic acid than the average, while the yield of alcohol from the maple exceeds by 20 per cent. that of the other woods. The wood employed in these tests was air-dried without bark, and in pieces 2 inches in diameter.

S. H. Collins<sup>1</sup> describes a portable form of wood distillation plant consisting of a cylindrical retort of  $\frac{1}{4}$ -inch boiler plate, 16 feet long, and 3 feet internal diameter, with an outer casing which forms part of the furnace for heating. The whole is mounted on wheels so that it can be moved from place to place. The condensing plant consists of a small tank where the tar condenses, and a cooling tank containing nine  $1\frac{1}{4}$ -inch iron pipes which are cooled by water. The collecting chamber is made from two 50-gallon barrels, each with a tap at the bottom and also a tap about the middle; the upper tap serving for drawing off the aqueous products of the distillation and the lower one for the tar. The whole apparatus is closed and works under slight pressure, the gases being conveyed from the second barrel by means of a pipe to the furnace. About 5 to 6 cwt. of firewood is required, in addition to the gas for distilling 1 ton of wood. One ton of hardwood yields about 5 cwt. of charcoal, 18 gallons of water which is thrown out, and 30 gallons of pyroligneous acid which is converted into acetate of lime in two tanks, and the solution of the latter is evaporated in an iron tray placed on top of the fire-box.

The following financial statement of the actual working of this plant will give some idea of its possibilities:—

# FINANCIAL STATEMENT

*Period—July 1st, 1914, to May 1st, 1916 (22 months)*

Receipts.	£	s	d.	Expenditure.	£	s	d.
11 tons 14 cwt. 1 qr.							
charcoal . . .	63	9	6	Wages . . .	61	8	11
Tar sold . . .	4	0	0	Lime . . .	1	13	6
In store—				Asbestos . . .	0	14	7
Charcoal . . .	10	0	0	Cartages . . .	1	11	7
Tar . . .	3	0	0		£65	8	7
Acetate . . .	10	0	0	Experimental . . .	70	0	0
	£95	9	6	Capital . . .	242	8	1
					£377	16	8

The retort is capable of taking a charge of 25 cwt. when packed full of solid blocks, but with loose irregular material only 12 cwt. can be put in at each operation. In full working the plant will deal with about 120 tons of wood per annum or about 3 tons per week for forty weeks, allowing twelve weeks for

<sup>1</sup> *Jour. Soc. Chem. Indt.*, 1917, p. 70.



bad weather. The complete distillation occupies usually about two days, but varies with the nature of the material, loose twigs requiring less. The temperature of the distillation is between 270° and 400° C.

The following analyses of charcoal from this plant show that the distillation is not a complete one:—

TABLE XVIII.—ANALYSES OF CHARCOALS

	Water.	Volatile Matter.	Fixed Carbon.	Ash.	Ash per cent. on Fixed Carbon.
Hardwood:—					
Elm . . .	3.77	20.15	73.88	2.20	2.98
Oak . . .	3.45	36.43	59.08	1.04	1.76
Ash . . .	4.02	19.10	75.30	1.58	2.10
Chestnut . . .	2.63	17.13	78.92	1.32	1.67
Sycamore . . .	3.56	27.66	67.34	1.44	2.14
Larch . . .	2.81	33.88	62.59	0.72	1.15
Barks:—					
Elm . . .	3.02	32.90	47.06	17.02	36.20
Oak . . .	3.87	42.37	47.64	6.12	12.85
Ash . . .	4.24	32.70	56.04	7.02	12.53
Chestnut . . .	3.42	25.14	64.37	7.07	10.98
Mixed Screenings	3.20	28.00	59.21	9.59	16.20

E. H. French and J. R. Withrow, in a paper read before the American Institute of Chemical Engineers, December 4, 1914,<sup>1</sup> traced the development of the wood distillation industry, and described the various types of plant in operation and their respective yields of products. At that time there were in operation in the United States fifty-three oven plants, capacity 2909 cords, thirty-one retort plants, capacity 593 cords, and six kiln plants, capacity 1300 cords daily, while in Canada there was one retort plant and nine oven plants, the former treating 48 cords and the latter 424 cords per diem. According to the authors the most successful results are obtained in ovens connected with tubular condensers. The size of these ovens being: height 8 feet 4 inches, length 26 to 54 feet, and width 6 feet 3 inches, and the cost of the plant \$2000 (about £420) per cord per day capacity. The products obtained in such ovens per cord (about 2 tons) of seasoned wood amount to 215 to 220 gallons of crude liquor containing 8 to 8½ per cent. of acid and 4 to 4½ per cent. of alcohol, 22 to 25 gallons of tar, 52 bushels (1040 lb.) of charcoal, and 11,000 to 12,000 cubic feet of gas, which in the early stages consists principally of air and carbonic acid, but later contains carbon monoxide and hydrocarbons so that it has then a con-

<sup>1</sup> *Met. and Chem. Eng.*, 1915, p. 30.

siderable value for heating purposes. The values of the products obtained from a cord of wood are given below:—

	£	s.	d.
Wood alcohol (82 per cent.) 11 galls. . . . .	0	11	5½
Acetate of lime 216 lb. . . . .	0	15	9
Charcoal 52 bushels . . . . .	0	14	1
	<hr/>		
The total cost of production being . . . . .	1	16	10½
	<hr/>		
And the profit . . . . .	0	4	5
	<hr/>		

*Treatment of the Products Obtained.*—As already noted, in the description of the products obtained in the carbonisation of wood, the liquid which flows from the condenser being at one time strongly coloured, and at other times pale, care is taken to “cut” the still at the moment it shows a pale brown colour, and a high percentage of acid as compared with the liquid which previously issued from the condenser, the same precaution being taken towards the end of the distillation, when the liquid again turns brown owing to the presence of a greater amount of tar. These products, besides their colour and percentage of acidity (which latter the workman can determine as often as necessary by means of a solution of normal soda), are easily recognisable by the smell. In the first stage the distillate, though almost free from acid and from tar, has a feeble empyreumatic odour due to the first disengagement of gas; in the second stage the distillate is dark, without, however, containing a large proportion of tar, and the quantity of gas produced is greater, but diminishes gradually thereafter, whilst as the third stage is entered the proportion of tar increases. Finally, in the last stage the amount of gas evolved falls considerably, while the distilled products flow more slowly from the condenser, and the goose-neck cools. By means of a series of gutters or pipes the condensed products at the various stages are run into different reservoirs, the upper portion of which is below the mouth of the condenser exit pipe, so that the liquids flow into them by gravity. These products, left to settle in the vats for some time, separate into three distinct layers, the lower layer consisting of tar charged with creosote oil and with acetic acid, the middle layer containing water, pyroligneous acid, wood-spirit, acetone, and some tarry matter held in solution by the aid of the other constituents, finally the upper layer, consisting of light hydrocarbons, still holding acetic acid in solution. The aqueous liquid is separated mechanically from the tars and from the heavy oils through taps placed at different levels; each layer is filtered through a bed of coarse sand, from which it flows into the appropriate receptacle, whence it is taken up by a pump and

transferred to reservoirs specially retained for these three products.

*Treatment of the Pyroligneous Distillate.*—The pyroligneous distillate, thus freed from the bulk of the oils, is afterwards run into stills to be separated into pyroligneous acid (or one of its compounds), wood-spirit, and tar. To effect this separation several methods are adopted. In some the liquid simply undergoes fractional distillation, in others the pyroligneous acid is neutralised by an alkali or an alkaline earth before it is distilled to separate the wood-spirit. Finally, in a third method of working the whole is distilled—water, wood-spirit, and pyroligneous acid; the condensed products being collected over lime, and then redistilled to separate the alcohol.

(1) *Simple Distillation.*—The vessels used to separate pyroligneous acid from wood-spirit are always made of copper; generally a still is used of 3 metres capacity, heated by open fire

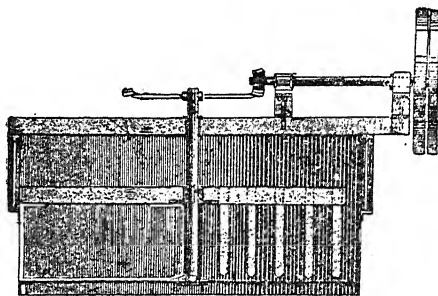


FIG. 19.—Mixing vat for neutralising the pyroligneous acid fitted with mechanical agitator.

or by steam. The first portion of the distillate, containing wood-spirit and acetone, with but little acetic acid, traverses three copper rectifying plates cooled on the outside by a small but regulated quantity of water. In this way a liquid rather rich in alcohol is obtained, which is collected in the crude alcohol tank so that it may afterwards undergo further treatment, which will be studied later. If it be merely desired to make pyrolignite of lime or pyrolignite of soda, the distillation is stopped when all the wood-spirit has passed over, then after cooling for some time the product is run off through a tap in the bottom; a mixture of water, acid, and tar runs off first, and is collected apart, then the pyroligneous acid, which is run into tanks, where it is saturated with carbonate of lime or carbonate of soda (Fig. 19). But if it be desired to produce pyroligneous acid to make pyrolignite (sugar) of lead, for example, the distillation is continued, taking care to separate the acid liquid, which condenses, and to run it into another reservoir. In all

cases when oily patches float on the condensed liquid the distillation is stopped, for nothing then remains in the still except tar, which is collected along with the other tar, to be treated later, for the extraction of creosote, for instance.

(2) *Distillation of the previously neutralised Pyroligneous Distillate.*—In this process, employed generally in the direct manufacture of pyrolignite of lime a predetermined volume of milk of lime, calculated on the amount of acid to be neutralised, is run into a still fitted with an agitator—the acid contained in

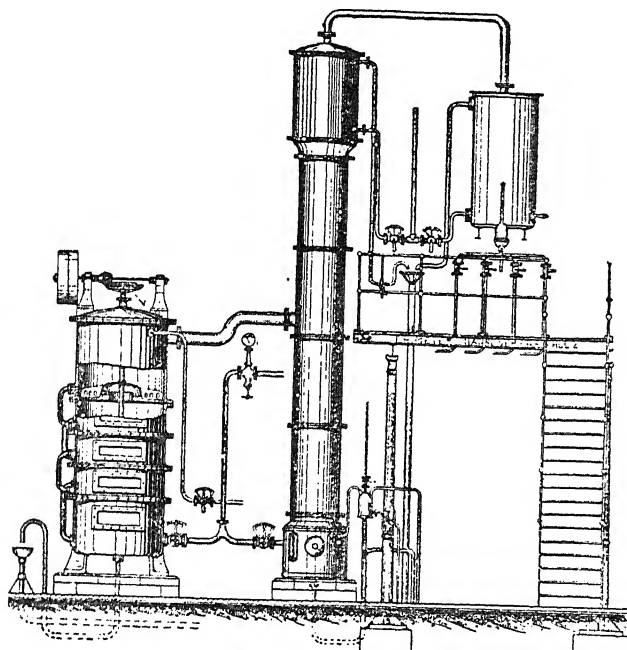


FIG. 20.—Sets of stills with mechanical agitators adapted for continuous working and connected with rectifying column for the distillation of the previously neutralised pyroligneous distillate.

the pyroligneous distillate having been titrated beforehand. After the mass has been well mixed and a test shows that it is neutral to litmus paper, the still is heated, preferably by steam, whilst the agitator is still kept moving. A mixture of water, methyl alcohol, and acetone distils; the liquid issuing from the condenser is collected in two stages, in one of the two tanks reserved for phlegms, thus separating the first running's phlegms from the last running's phlegms as soon as the condensed liquid becomes milky. The distillation is finished when a sample of the distillate, examined by the alcoholometer, shows

no presence of alcohol. The residue in the still is then run into the evaporating pans, where it is concentrated preferably by the waste heat of the furnaces. When it is desired to convert pyroligneous acid into pyrolignite of soda, it is often separated from the wood-spirit by distilling the crude liquid—freed from tar—consecutively in two pans connected with each other; the second pan, fitted with an agitator, contains calculated quantities of lime and of sulphate of soda dissolved in water, the amounts being determined after titrating the pyroligneous acid introduced into the first pan. The acid products distilled from this pan by a steam coil are converted in the second pan into acetate of soda, owing to the affinity of the sulphuric acid of the sulphate of soda for the lime, whilst the alcohol, acetone, and their non-acid derivatives are again distilled and condensed. The distillation being finished, the mixture from the second still is run into a wrought-iron reservoir, where it deposits the sulphate of lime produced in the process; the clear liquid is then run off and evaporated. In the three-pan system the pyroligneous distillate is heated by steam in a first still of a capacity of about 10,000 litres (2200 gallons); the distilled products are collected in milk of lime contained in a second pan, in which the methylic acetate is decomposed, forming acetate of lime, likewise also the free acetic acid which passes over. The wood-spirit again distils and afterwards passes through a milk of lime in a third pan, where the decomposition of the traces of methyl acetate which might have escaped the first reaction is terminated. Finally, steam and methyl alcohol run into the coil of the condenser. When the liquid which flows from the condenser marks zero on the alcoholometer the third pan is cut out, the vapour from the second allowed to escape into the open air, until that from the first pan is no longer acid, which indicates the end of the operation.

(3) *Complete Distillation of the Pyroligneous Distillate.*—By an alternative arrangement of the above process the distillation may be made practically continuous. Two stills of 6000 litres capacity (1320 gallons), working in turns and heated by a steam coil, are charged from a higher level with the pyroligneous products to be distilled. The still which is at work communicates with a No. 1 pan of 2500 litres capacity (550 Imperial gallons) charged with milk of lime; No. 1 pan communicates with a No. 2 pan exactly similar, and which, moreover, is in communication with the condenser. The vapours (steam, pyroligneous acid, wood-spirit, acetone, etc.) which come from the still charged with pyroligneous products, are led by a pipe pierced with holes to the bottom of No. 1, which retains the bulk of the acid products; as No. 1 is also heated, distillation also takes place here, the distilled products, still containing pyroligneous acid, bubbling into

the milk of lime in No. 2, which should only allow acid-free substances, like wood-spirit and acetone, to pass through it. These are liquefied in the condenser, from which they pass to a special reservoir, the liquid collected in which then contains 30 to 40 per cent. of alcohol. The contents of No. 1 pan are controlled by taking a sample from the test tap from time to time, and as soon as the test shows a slight acidity, showing that all the lime has been neutralised, No. 1 pan is isolated by manipulating the connecting taps so as to put the still in direct communication with No. 2. Then No. 1 is emptied of its contents, which are run into a storage vat. No. 1 is then

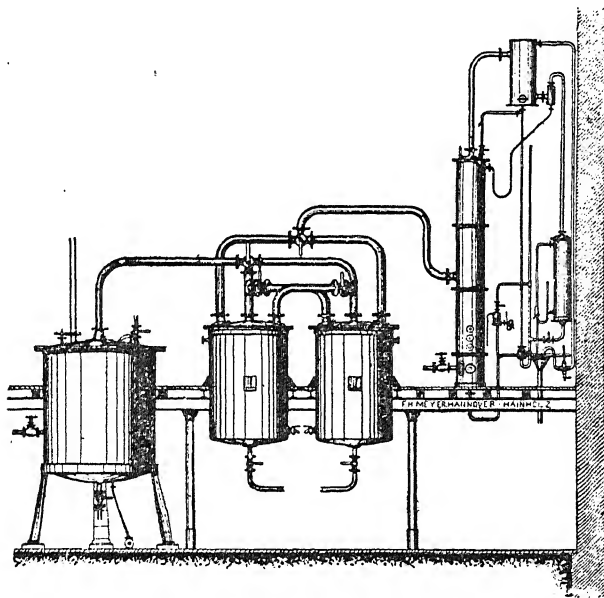


FIG. 21.—Group of three stills for continuous working with rectification plant for the complete distillation of the pyroligneous distillate.

charged with fresh milk of lime, and brought in turn, by opening the necessary taps, as the No. 2 pan, for the absorption of acid vapours. The vapours from No. 2 pan, free from acid, pass to the condenser or into a distilling column, in which the methyl alcohol is concentrated (Fig. 21). When the whole of the acid and consequently the alcohol has been expelled from the first still, a fact which is ascertained by testing, it is disconnected from the milk of lime pan, which is then connected with the second still, which is at once put into operation. For the transfer of the crude pyroligneous distillate, pumps or monte-jus are preferable to injectors, which have the defect that they are liable

to become obstructed by the tar which remains suspended in the liquid and might perhaps occasion serious accidents to the distilling plant. In fact, if the pipe which brings the pyroligneous distillate from the injector be obstructed, steam alone continues to pass into the pan until the moment when the pipe begins to clear itself, whereupon the liquid suddenly runs into the pan, and cooling the latter, a comparative vacuum is formed, which results in the pan being crushed.

*Pyrolignite of Lime. Treatment of the Acetate of Lime Solution.*—Pyrolignite of lime, together with methyl alcohol and charcoal, are the most important products of a wood charcoal factory. Great care, therefore, must be exercised in its manufacture, not only to reduce loss in manufacture as far as possible, but also to obtain a product as rich as possible in acetic acid (60 and even 65 per cent.), containing at the same time a minimum of free lime and tarry matter, the latter giving rise to some

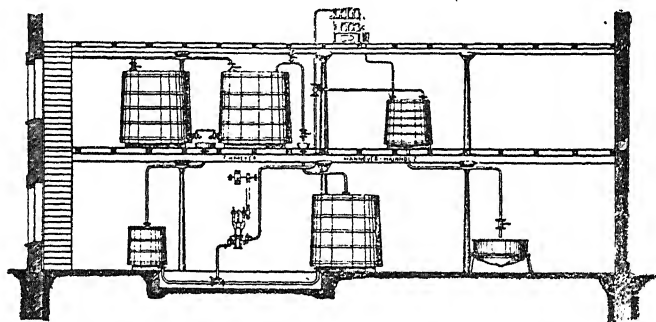


FIG. 22.—Installation of clarifying and evaporating vats and filter press for acetate of lime manufacture.

difficulties in the manufacture of commercial acetic acid. This, it is hardly necessary to explain, is why the manufacturer separates the condensed products obtained in wood charcoal manufacture into respectively: (a) pyroligneous products for grey acetate of lime manufacture, and (b) pyroligneous products for brown acetate of lime manufacture, the amount of acetic acid in the latter not exceeding 45 per cent. The solutions of acetate of lime are allowed to stand for some days in wooden vats (Fig. 22), in which they separate from the tar and mud held in suspension. The clarified solution is then drawn off and pumped into one of the reservoirs, feeding the evaporating stills, whilst the muddy portion is passed through the filter presses, the filtrate from which is mixed with the clarified solution. The wash water, from washing the cakes in the filter presses, is utilised for making milk of lime. The 20 per cent. acetate of lime solutions cannot be evaporated and set aside to crystallise like an ordinary

mineral salt; therefore different systems of concentration are used to convert it into a commercial, and more especially a transportable, product. In some factories it is evaporated in hemispherical cast-iron pans heated over a naked fire; during the whole of this operation, in consequence of the action of the air on certain organic matters, tarry scums form on the surface of the liquid, which have to be skimmed off, in order to facilitate evaporation. When the solution reaches  $15^{\circ}$  B. ( $23^{\circ}$  Tw.), specific gravity 1.115, a crust of acetate of lime becomes attached to the sides of the pan. This crust must be removed to prevent the decomposition of the salt by overheating. Finally, when the whole mass is sufficiently evaporated and has a pasty consistency, the fire is withdrawn from below the pan, the drying being then finished, treating small quantities at a time in two flat cast-iron pans continuously heated by the same furnace. In these pans the salt is constantly stirred by an iron spatula to

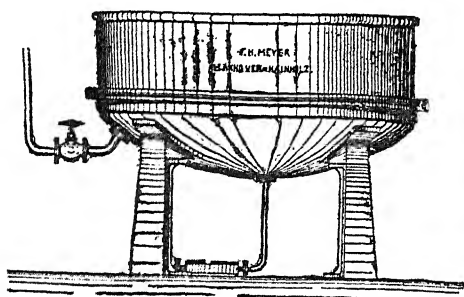


FIG. 23.—Steam-jacketed pan for evaporating solutions of acetate of lime.

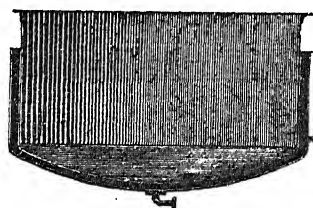


FIG. 24.—Steam-jacketed pan for evaporating solutions of acetate of lime, section.

avoid any decomposition. The acetate of lime undergoes preliminary drying in the pan farthest from the fire, then it is placed in that directly over the fire, where the drying is finished, whilst the first pan is refilled with paste in order to start a fresh charge. Certain manufacturers prefer to lift the crystalline crusts, which form in the evaporation of acetate of lime solutions, by a shovel. These crusts are laid to drain in a basket placed above the pan, to be afterwards dried and piled on a cast-iron sole-plate, heated by the waste heat of the distillation furnaces. In this process, pending the final drying, which takes place in the hottest part of the stove, care is taken to stir the acetate continually by means of special appliances, so as to crush the salt and to prevent it from agglomerating on the sides of the pan. In another process the pans are arranged in ascending order directly over a fire; the one farthest away is used to concentrate the acetate of lime, whilst the pans nearer the fire dry



the salt completely. This plan, which requires much space and does not sufficiently prevent the decomposition of the acetate of lime, is often modified by the use of steam-heated, jacketed, copper or wrought-iron shallow pans of 2000 litres (440 gallons) capacity (Fig. 23). Steam coils are not suitable for this class of evaporating pan, for they render the stirring of the mass difficult,

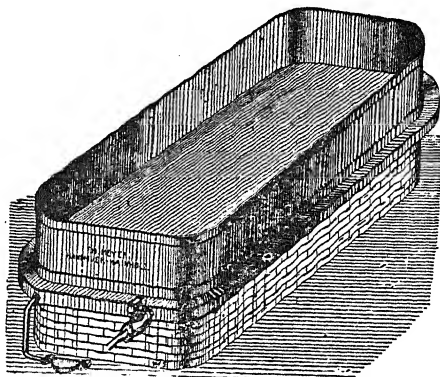


FIG. 25.—Shallow pan heated by coil for evaporating acetate of lime.

especially when the pellicles of acetate of lime begin to form. Round, wrought-iron or rectangular pans with cast-iron bottoms and coils (Figs. 24, 25, 26), issuing from the cast-iron bottom, are likewise successfully employed.

The evaporation of the solution of acetate of lime in this kind of pan proceeds comparatively quickly up to 40 per cent. using ordinary steam, but it is then necessary to stir the mass

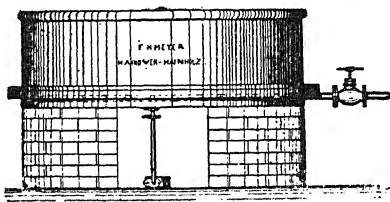


FIG. 26.—Shallow pan heated by coil for evaporating acetate of lime.

with mechanical agitators; for that purpose small pans requiring less power, because the mass to be set in motion has less bulk, will be chosen in preference to large pans, which require a greater expenditure of steam, not only to drive the mixer but to finish drying. It is better not to complete the desiccation in these pans. When the acetate of lime turns brown and becomes pasty between the fingers without adhering, it is dried completely by projecting it on to cast-iron plates heated to redness

by the gases from the furnaces of the wood charcoal retorts. Acetate of lime may also be drained in the concentrated pasty condition in stoves, heated by a current of hot air, the circulation of which is facilitated by fans, or the acetate of lime may be spread in thin layers on wrought-iron plates heated by a special furnace, the gases from which circulate in winding flues. By this process the still moist acetate of lime, being placed above the furnace itself to avoid overheating, winds round with the flues so as to give to these torrefiers the form of a gridiron. The torrefaction is intended in the first place to eliminate the last trace of water, in order to produce an 80 per cent. acetate; in the second place it removes the volatile tar oils, which, unless this were done, would impart a dark brown colour and empyreumatic odour to the acetate of lime. As soon as the acetate of lime has assumed its grey colour and is easily reduced to

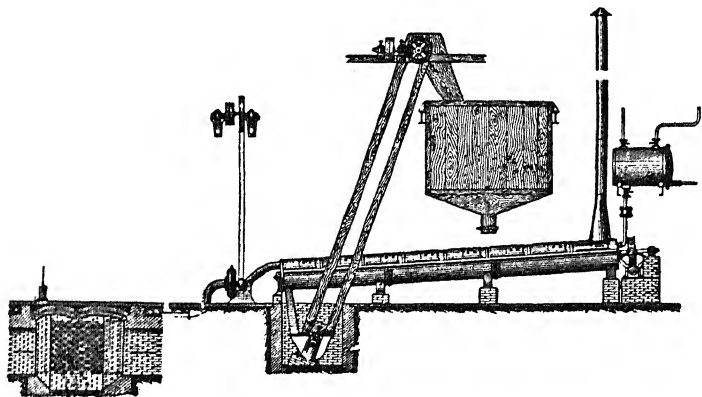


FIG. 27.—Drum drier for acetate of lime.

powder between the teeth, torrefaction is complete; the product is then crushed to small lumps by means of rollers. The installation of a mechanical drier (Fig. 27) in the form of a drum, requiring comparatively little labour, has the advantage of yielding a more uniform product without waste, due to the carrying away by the air of dust formed during drying. The acetate of lime to be dried is led into the drum by the extremity opposite to that through which the hot air enters, and is kept in motion by a helix, which moves in the cylinder and is surrounded by hot air. As it issues the acetate of lime is raised by the cups on the elevator to a floor above, into a sort of wooden bin, from which it is bagged up into sacks of 50 and 70 kilogrammes (110 and 154 lb.). This acetate of lime is the grey acetate of lime of commerce; it contains about 10 per cent. of water, a maximum of 84 per cent. of pure acetate of lime, and 6 per cent.

of foreign substances: tar, lime, carbonate of lime, etc. Of the 10 per cent. of water 4 to 6 per cent. may be eliminated at  $150^{\circ}$  C. ( $302^{\circ}$  F.), and most of the remainder at a higher temperature, but there would be no advantage in attempting to exceed an acetate content of 80 to 82 per cent., because it would simply lead to a loss in the yield; this product commencing to decompose at  $150^{\circ}$  C. ( $302^{\circ}$  F.).

*Brown Acetate of Lime.*—This salt is obtained by saturating the dark brown pyroligneous distillate from wood by lime. As the liquid contains dissolved tar, it follows that the brown acetate so obtained has a much lower acetate of lime content (only 45 per cent.) than the grey acetate. This acetate, being less easily decomposed by mineral acids than the grey acetate, and moreover since it yields a cruder acid, the value of the acetic acid made from it is less than that of the acetic acid made from the grey acetate.

## CHAPTER III

### THE ACETIC ACID INDUSTRY

*Acetic Acid from Acetate of Soda.*—Formerly acetic acid was made by wood distillers; they first converted the acetate of lime into acetate of soda, as previously indicated, or prepared acetate of soda directly by neutralising the pyroligneous distillate with carbonate of soda. The soda solution was concentrated so as to obtain crystallised acetate of soda, which was separated from the mother liquors. This purified salt, known in commerce as "red salt," on account of the traces of tar and the higher homologues of acetic acid which it contained, was decomposed by sulphuric acid yielding a liquid containing 50 per cent. of acetic acid. This product, on account of the empyreumatic substances which it contained, could not be used as an ingredient of food. To obtain the acid in a purer state, the "red salt" was fused in its water of crystallisation by heat; the butyrates and propionates being thus decomposed, the acetate of soda was dissolved in water and again crystallised. By a second fusion of the salt, followed by a fresh crystallisation, a chemically pure salt was obtained, from which pure acetic acid could be extracted by decomposition by sulphuric acid. It was only the progress made in industry which led manufacturers to produce different qualities of acetic acid capable of being used for various purposes. At present commercial acetic acid, termed acetic acid for industrial purposes (*acide acétique des arts*), the chief uses for which are the manufacture of verdigris, chrome yellow, white lead, aniline, etc., is prepared from acetate of lime, the presence of certain organic matters which accompany it having no injurious effects.

*Acetic Acid from Acetate of Lime.*—The mineral acids used to decompose the acetate of lime are: (1) commercial hydrochloric acid; (2) commercial sulphuric acid of 60° to 66° B. (142° to 168° Fw.), specific gravity 1.715 to 1.84. The two processes are both used, the selection depending on the quality of acid desired and the circumstances in which the manufacturer is placed, facility for purchase of raw materials, outlet for acetic acid produced, etc. In fact, of the product which it is desired to manufacture, the following strengths and grades are required: (1) commercial acetic acid of 38, 60, or 75 per cent.; (2) concentrated

commercial acetic acid of 85 to 100 per cent.; (3) fine flavoured acetic acid (*acide acétique bon goût*) for dietetic purposes, free from metallic compounds and empyreumatic products; (4) chemically pure acetic acid (glacial) of 96 to 100 per cent. For the production of industrial acid, the commercial hydrochloric acid process is preferred, being much more economical than the sulphuric acid process, which always requires mechanical agitators.

(1) *Hydrochloric Acid Process*.—The manufacture of acetic acid by means of hydrochloric acid may be carried out in two ways: the first, which is the oldest and still the most used, was discovered almost simultaneously by Winkel and Christi. It consists in mixing hydrochloric acid with the acetate of lime; and allowing the products of the reaction to settle for twelve hours. A wooden vat or pit built of masonry and fitted with an agitator may be used. For 100 kilogrammes (220 lb.) of acetate of lime, is required, according to its acetic acid content, from 95 to 115 litres (20·9 to 25·3 gallons) of hydrochloric acid of 20° to 21° B. (32° to 34° Tw.), sp. gr. 1·16 to 1·17. The acetate of lime being in the vat, the acid is run up on it and the whole stirred until it is completely fluid; it is then left to stand for several hours. A certain amount of tarry matter separates, which rises to the surface of the liquid and is removed with a large skimmer. The solution of chloride of calcium formed in the acetic acid, of a density of 1·250, is then run into a still, consisting of a copper pan heated by naked fire or by an open steam pipe and a closed steam coil, which are fitted in the interior. This apparatus is in communication, by a rather wide pipe, with a copper or, better still, a tin condenser.

If heating be done by steam, distillation is commenced by passing waste steam from the pumps or the engines through the coil; about 50 per cent. of the product is distilled in that way; then direct steam is turned on through the "blow-up" pipe; the steam carrying over the rest of the acetic acid, leaving in the still an aqueous solution of chloride of calcium and tarry matter, rendered insoluble in consequence of the removal of the acetic acid. This residue is then run out through a pipe situated in the lower part of the apparatus. The acetic acid obtained by this process contains from 40 to 45 per cent. and may be used for many purposes; but when intended for certain industries which require it free from chlorine, it has to be re-distilled with a small amount of lime (the proportion of which has been determined from the titration of the chlorine as silver chloride). This operation is conducted in a still similar to the foregoing, but capable of being heated by a steam jacket. As the products which distil in the beginning and at the end of the operation are milky, from the empyreumatic oils which they

hold in suspension, they are separated from the middle runnings and allowed to stand; after running off the oils, which float to the top, the acid is mixed with the products to be rectified in a fresh operation. By the distillation of 100 kilogrammes of 82 per cent. acetate of lime, 60 kilogrammes of acetic acid of 100 per cent. strength should be obtained, but this result is never quite realised, because the solution of chloride of calcium always retains a little acetic acid, the cost of extraction of which would exceed its value.~ When 85 to 100 per cent. acid is desired, a copper rectifying column (Fig. 28) consisting of a cylindrical pan of about 8 mm. (say  $\frac{1}{4}$  of an inch) thick, with an average capacity of 3000 litres (660 gallons) and heated by a steam coil is used. The column is similar to that of an ordinary alcohol

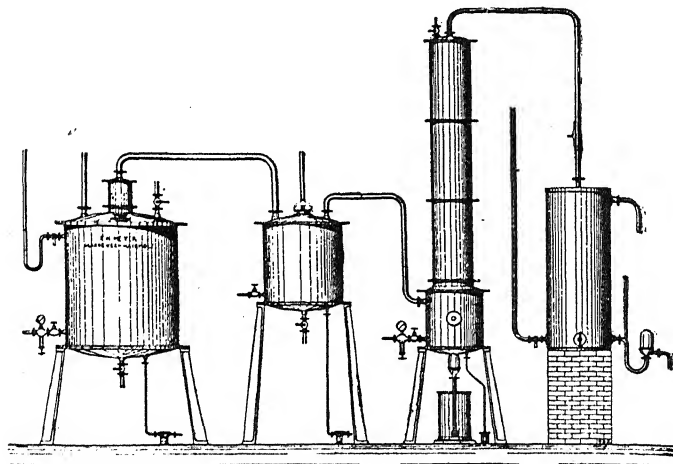


FIG. 28.—Plant for the continuous manufacture of commercial acetic acid of 85 to 100 per cent. strength.

rectifier, in which copper plates are replaced by porcelain or earthenware plates. The strength of the acid as it issues from this column is higher the weaker the current of water which circulates on the plates, and, as it is generally desired to obtain the crystallisable acid, not because it is more valuable but because it is purer (the presence of the vapour of water in the distillation aids in the carrying away of propionic and butyric acids), the flow of water on the plates should be regulated so as to collect, after a short time, crystallisable acid of 96 per cent. strength: 100 lb. of 45 per cent. acid yield on rectification 25 to 30 per cent. of 96 per cent. acid, and 75 to 80 per cent. of 20 per cent. acid. The distillation of acetic acid in solution with chloride of calcium may also be carried out continuously accord-

ing to Boessneck's process. In this case the solution, previously warmed in a copper pan, flows in a continuous manner on to the upper part of a column apparatus. As it falls from plate to plate, and becomes more and more heated, the acetic acid separates and passes into a condenser, where it is liquefied, whilst a solution of calcium chloride flows away from the bottom of the column. The strength of the acid obtained in this way is 45 to 50 per cent. and it is of sufficient purity for general use.

(2) *Sulphuric Acid Process*.—In this process the plant employed is altogether different from the preceding, because mechanical mixers, which were not required for the distillation of the mixture of acetate of lime and hydrochloric acid, since it always remains fluid, become indispensable by the use of sulphuric acid which yields an almost solid mass with acetate of lime. Another peculiarity of this process is that sulphuric acid, acting in an aqueous medium, gives rise to secondary reactions; in fact, owing to the heat disengaged, but still more to the heat radiated from the masonry surrounding the pan, since it is heated by naked fire, sulphurous acid (arising from the action of the sulphuric acid on the tars) is generated; moreover, the oils present in the pyrolignite of lime distil with the acetic acid. The crude acetic acid obtained by the use of sulphuric acid is, therefore, more impure than that made by the aid of hydrochloric acid, but it has the benefit of being more concentrated, which may be readily understood when we take into account the fact that strong hydrochloric acid contains upwards of 60 per cent. of water. One hundred lb. of pyrolignite of lime, containing 86 per cent. of pure acetate of lime, contains 10 per cent. of water and the 60 lb. of sulphuric acid, theoretically necessary, brings 7 lb. of water; upwards of 70 lb. of 85 per cent. acid should be collected, but this result is never obtained, especially in distillation with access of air by direct heat, and still less if only the theoretical amount of sulphuric acid be used in the reaction. In fact, to prevent the acetate of lime from being attacked by the sulphuric acid and thus converted into acetone, an excess of 8 to 10 lb. of sulphuric acid per 100 lb. of lime should be added to replace the acid which is converted by the tar into sulphurous acid, as already mentioned. The acetic acid obtained, termed *acide acétique des arts* (commercial acetic acid), is only about 75 per cent. strength, because it contains not only the water brought by the sulphuric acid and the pyrolignite, but also that coming from the reduction of the sulphuric acid by the tar.

*Merits and Defects of the two Processes*.—Besides the difference in the acetic acid content of the products obtained by the two processes, that by hydrochloric acid yielding 45 to 50 per cent. instead of 75 per cent. by the second, it is to be noted that

the sulphuric acid process entails a larger consumption of fuel, to develop the power required to drive the mixers, without taking into account that the proportion of sulphuric acid required is greater than theory, which is not the case in the hydrochloric acid process. On the other hand, the weight of raw materials with which the vessels are charged must be less in the second process than in the first, hence increase in manufacturing expenses, but on the other hand, after the distillation of the acetic acid produced by the decomposition of pyrolignite by hydrochloric acid, a fresh distillation of the acetic acid may be necessary to produce a product free from the volatile mineral acid. The question which acid should be used will depend upon cost and

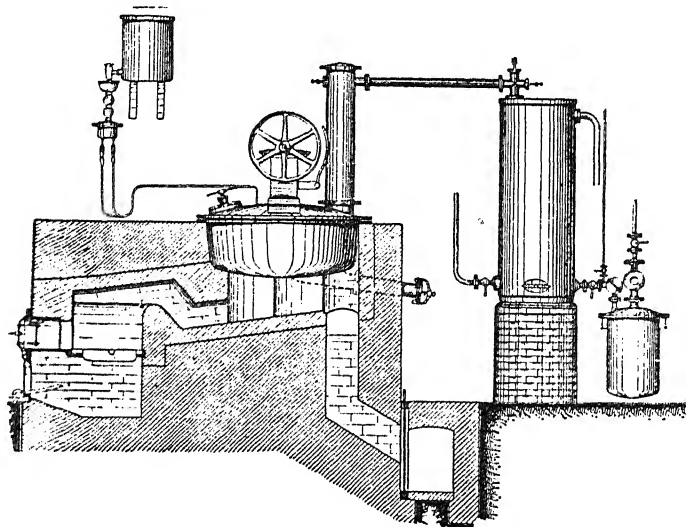


FIG. 29.—Plant for the manufacture of acetic acid by the sulphuric acid process under atmospheric pressure.

the uses to which the residuals can be put. Calcium chloride can be used for refrigerators, and for laying dust on roads and in coal mines. Calcium sulphate is almost valueless, but could be used on land poor in lime. It follows from these considerations that when it is a question of producing industrial acetic acid it may be preferable to use sulphuric acid. The plant used for the manufacture of acetic acid, by the decomposition of pyrolignite of lime by means of sulphuric acid, consists of a flat cast-iron pan heated by a naked fire (Fig. 29). This pan, built into the masonry of the furnace, has a pipe let in at the bottom through which the residue may be evacuated when the operation is finished. An agitator with blades keeps the mass in motion from the commencement of charging, first with pyrolignite of



lime, then with sulphuric acid, until the operation is terminated. The acetic acid distilled, after having traversed a dust chamber, passes to a condenser, where it is condensed.

*Van der Linden's Process.*—This process (French patent 248,056, January 10, 1895, with certificate of addition of April 14, 1896; German patent 92,418, class 12, deposited November 29, 1894) is a very ingenious modification in the process for the manufacture of acetic acid from pyrolignite of lime or other acetate and sulphuric acid (Figs. 30, 31, and 31A).

The distillation is conducted under reduced pressure, steam heat instead of a fire being used for heating. Under reduced

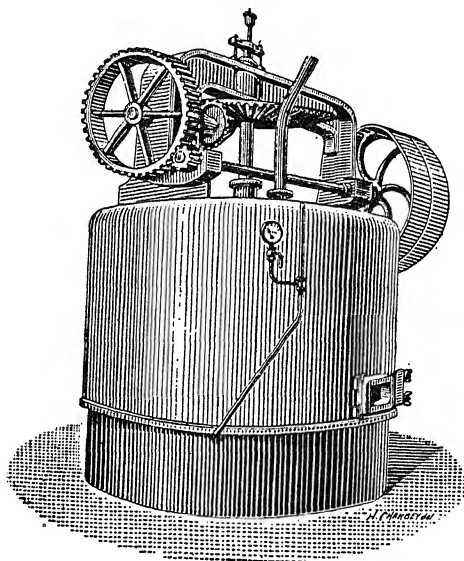


FIG. 30.—Apparatus for the manufacture of acetic acid by Van der Linden's process.

pressure the acetic acid distils at a lower temperature, the advantages of which are that (1) secondary products due to the action of the sulphuric acid on the oils or tars in admixture with the pyrolignite of lime are avoided; (2) a smaller amount of sulphuric acid suffices than when distillation is conducted under the ordinary atmospheric pressure, the amount nearly approaching the theoretical quantity of sulphuric acid required for a complete reaction. The acetic acid obtained is therefore purer since it contains no empyreumatic products. Moreover, capacious vessels may be used, capable of treating much larger quantities, as in the hydrochloric acid process, for example, and also either brown or grey pyrolignite of lime may be dealt with.

*Behren's Process.*—Consists in mixing pyrolignite of lime with acetic acid and then treating the mixture with sulphuric acid. It is thus possible, by diluting the mass, to use only the theoretical amount of sulphuric acid required to decompose the acetate without producing secondary reactions. One hundred parts of acetate of lime of 81 per cent. strength is stirred into 100 parts of acetic acid, then the theoretical quantity of sulphuric acid is added, say 55 parts of 92 per cent. monohydrated acid. The mass having been well mixed, it is passed through

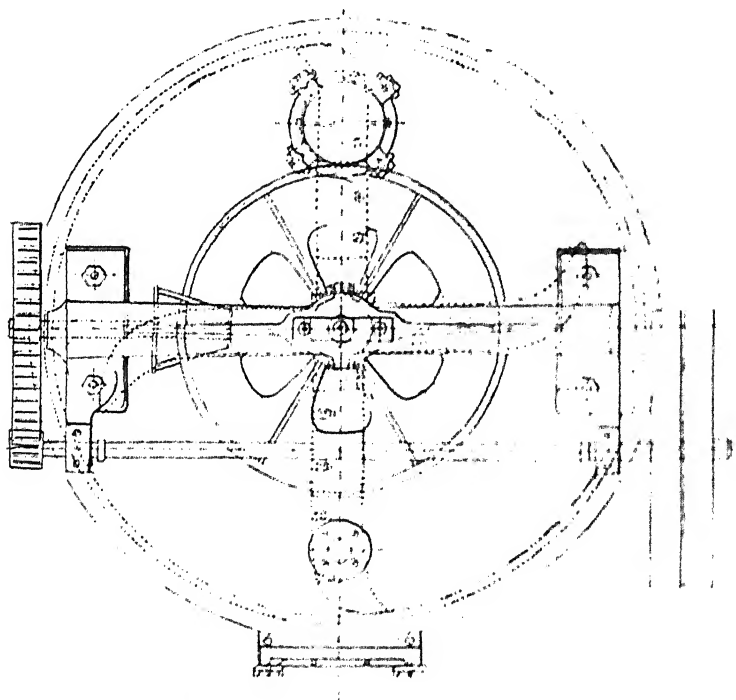


FIG. 31.—Apparatus for the manufacture of acetic acid by Van der Lauden's process, cross section.

a filter press; the liquid which flows away is acetic acid, sufficiently concentrated to be used in the manufacture of glacial acetic acid; as to the residue it is gypsum.

*Installation of an Acetic Acid Factory. Description of a Factory treating Pyrolignite of Lime by Sulphuric Acid and afterwards Rectifying the Acid Product obtained.* Such a factory will be situated at a reasonable distance from inhabited houses, so as not to incommode the neighbours by the strong smell given off by the residuals as they are being discharged. The pans used for making commercial acetic acid are of cast iron

They are fitted with an agitator, and are heated by masonry furnaces or by steam; in the first case, so as to ensure uniform heating, the dimensions of the pans constructed to treat 500 kilogrammes (say  $\frac{1}{2}$  ton) of pyrolignite of lime; whilst, in the second case, pans taking a charge up to 1500 kilogrammes (say  $1\frac{1}{2}$  tons) may be used. There is a manhole in the top of the pan, through which the pyrolignite of lime is fed. Above the decomposing pans is a floor, which serves as a store for the

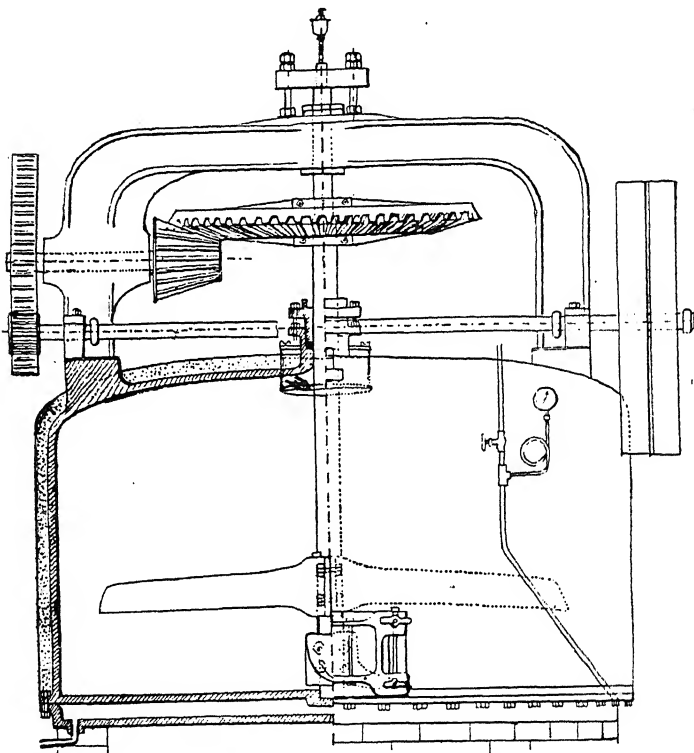


FIG. 31A.—Apparatus for the manufacture of acetic acid by Van der Linden's process, vertical section.

acetate of lime received in sacks of 50 to 70 kilogrammes (110 to 154 lb.). The pans are directly charged with pyrolignite, by shooting the contents of the sacks through openings in the floor, by the help of wooden hoppers. The pan being charged with acetate, the manhole is closed, and the agitator set in motion (Figs. 30 and 31); then, through a lead pipe, the sulphuric acid, contained in a lead-lined gauge tank, connected to the apparatus, is run in. The flow of sulphuric acid should

be gentle, so as to produce a very intimate mixture, and thus avoid solidification, which might cause the mixer to stick. Soon after the sulphuric acid reaches the mass heat is evolved and the acetic acid begins to distil, even with a somewhat low fire, which is kept up for some time after having run in the sulphuric acid. Next to the pan is an apparatus called a dust compartment, 60 cm. wide by 1.3 metres deep ( $23.4 \times 51.7$  inches), placed on a floor at a higher level than the pan, so that the products which condense therein may fall back into the distilling apparatus. This dust chamber is constructed of lead, lined inside with large earthenware pipes, which protect the lead from the action of the acetic acid. From thence the vapours pass through a tin (not tinplate) junction to the condenser, consisting of a copper (or better, a tin) coil, laid in a wrought-iron tank, in which cold water circulates. The condensed acetic acid flows into a drum, of the same metal as the coil, surmounted by a pipe, which leads the uncondensed products to the chimney, whilst the liquid is siphoned into the reservoirs, passing through a vessel into which all the liquid distillates from the pans pass, so that the liquid being distilled from any pan, the working of which has to be supervised, can be examined at any moment. An operation lasts about seven hours. In the Van der Linden process, the acetic acid from the condenser flows into a glass flask, then into a tin pipe, which leads it into earthenware reservoirs similar to those used in the manufacture of nitric acid, the bottoms of which communicate with each other by a pipe, on which a gauge glass is fixed, by a T-piece, which is also in communication with the upper part of the condenser, the condensation, like the distillation, taking place under reduced pressure. Two others of the upper pipes of the series of condensers are branched; on one pipe the branch connects with the vacuum pump, and on the other with the vacuum indicator, which is preceded by a short-necked bottle containing crystallised carbonate of soda, so as to preserve the metallic parts from the action of the acetic acid. The vacuum is brought to bear on the condenser by a series of earthenware taps, and through that also on the distilling pan itself. In the same way, the condensers may be isolated, when needful, as at the end of the operation, to re-establish atmospheric pressure inside the pan, or in the condensers when it is desired to extract the acetic acid. Between the earthenware condensers and the vacuum pump, scrubbers are fixed, consisting of at least two cast-iron columns 70 cm. ( $27\frac{1}{2}$  inches) in diameter by 3 metres (10 feet) high (Fig. 32), in which are fixed wooden or earthenware plates, supporting wood fibre moistened with a solution of carbonate of soda of  $10^{\circ}$  B. ( $15^{\circ}$  Tw.), sp. gr. 1.075; this solution is introduced by the vacuum to the top part of the

column, and the wash liquor from these scrubbers, containing as it does acetate of soda, is used in the manufacture of that salt. As soon as all the sulphuric acid has been charged into the still, the disengagement of acetic acid slackens; the mass must

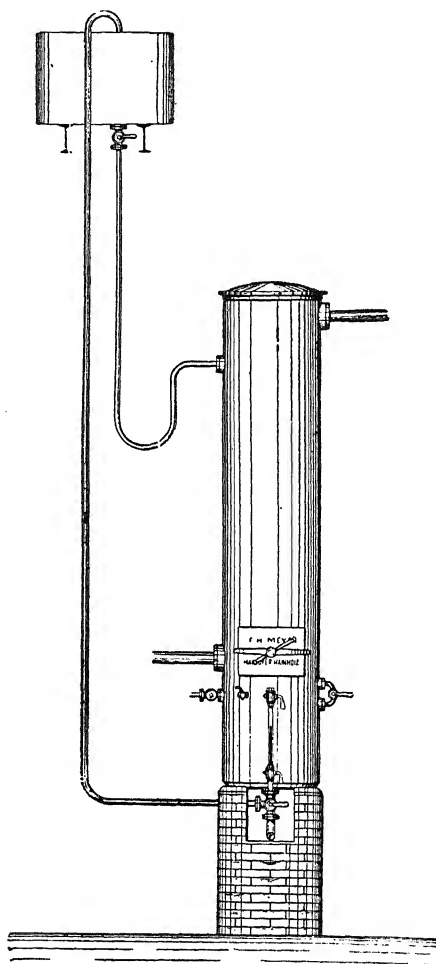


FIG. 32.—Wash column scrubber for the condensation of acetic acid vapours.

therefore be heated in order that the acid may distil in a continuous stream, until the operation is terminated, a point which may be ascertained by the amount of acetic acid condensed, and by the flow from the condenser passing into the glass flask only drop by drop. The fire is then banked up with ashes, steam is

turned off, the manhole above the bottom of the apparatus is opened, still keeping the stirrers working so as to run out the sulphate of lime into a gutter common to all the mixers, in which an Archimedean screw revolves, carrying the residues into a close chamber, where they cool for several hours, so as to avoid the disengagement of bad smells due to empyreumatic products and to the acetic acid vapour which remains in the still. The condensed acetic acid is propelled, either by a monte-jus, or by a rotary bronze pump, into different wooden reservoirs. In some of these it is brought, by the addition of water, to the commercial strengths ( $30^{\circ} = 28$  per cent. ;  $40^{\circ} = 38$  per cent. ;  $60^{\circ} = 56$  per cent. ;  $70^{\circ} = 65$  per cent. ;  $80^{\circ} = 75$  per cent. ;  $85^{\circ} = 80$  per cent.—all approximately). From these reservoirs, the acetic acid is drawn into wooden casks for delivering to the different firms who utilise it. Other reservoirs are also used to feed the acetic acid rectification plant.

*Rectification of Acetic Acid.*—The object of this operation is to produce acetic acid free from sulphuric acid and of a still greater strength than that obtained in the original distillation. The apparatus used is a column rectifier, similar to that used in alcohol distillation. It consists, in fact, of a horizontal copper pan (this metal protected from air being very little attacked by organic acids) of a capacity of 3000 to 5000 litres (660 to 1100 gallons). One of the bottoms is capable of being readily removed, so that repairs can be easily executed, if need be, say to the steam coil by which the plant is heated. A vertical jacketed still is also used in the rectification of acetic acid, but it requires to be constructed in quite a special manner, so as to be easily repairable. The lid has a disengagement pipe in the centre and a manhole for cleaning the apparatus (Fig. 33). The column which forms the continuation of the copper still is likewise of that metal, but with porcelain or earthenware plates, which are naturally more resistant than copper. The coil of the condenser is sometimes also of porcelain, but, this being very fragile, it has to be fixed with the greatest of care. Cast-iron pans, the price of which is about the same as copper ones, are not to be recommended, because they are difficult to repair, and when worn out they are worth next to nothing, compared with copper pans, which, when they are not usable, may still be sold by weight. As soon as the acid is run into the pan heat is applied slowly, so that gases such as sulphurous acid may escape at the beginning. Then the steam in the coil is increased up to the moment when the acid vapours, passing into the column, begin to liquefy at the condenser. The heat applied to the pan and the water run on to the column, are then regulated by the strength of the acetic acid which it is desired to obtain. The first portions distilled contain the acetic, methylic, and sulphurous acid

products, which are collected apart, and when the acetic acid, which condenses, titrates 96 per cent., it is collected in the crystallisable acid reservoir. However, as the acetic acid obtained by this operation still contains empyreumatic products and traces of copper, if a purer acid be required, it must be rectified once more, previous to which it may be purified by the use of permanganate of lime in solution, which is made to act on the acetic acid contained in earthenware tanks. This treatment by permanganate is followed by fresh distillation in a copper pan, heated by a steam coil, the distilled products being condensed in

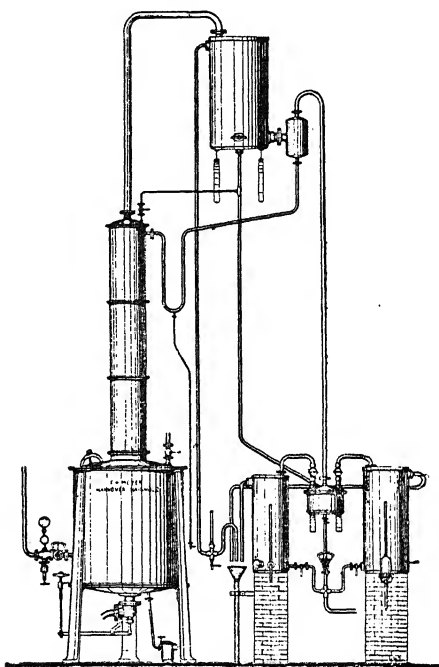


FIG. 33.—Rectifying column for acetic acid vapours.

an earthenware or in a silver coil, the latter being expensive but much less fragile. The residue from the rectification plant, of a more or less dark colour, consists in great part of acetic acid (along with which there occur the homologous acids contained in the acetate of lime) and tars; these residues are led into a reservoir, where they are allowed to settle, so as to separate the acid which they still contain, which then undergoes further treatment. To prevent the entrance of air into the apparatus effectively, the emptying of the rectifier should be done as rapidly as possible, not letting it cool too much before a fresh

charge. In the installation of an acetic acid factory the wooden vats are located in a building adjacent to that in which the acetate of lime is decomposed and the acetic acid rectified; the piping of these vats is of tin or copper according to the quality of the acid conveyed therein. Finally, in winter care is taken so to heat this building in order that the crystallisable acid may not solidify. In addition to the different working departments, a building must be reserved for the engines, in which a dynamo for electric light is installed. An acetic acid factory, using the sulphuric acid process without a vacuum, producing about half commercial acid and half pure acid, expends about 250 kilogrammes (550 lb.) of coal per ton of pyrolignite of lime treated.

*Glacial Acetic Acid.*—Besides the crystallisable, *i.e.* glacial, acid described in the previous chapter, this product may also be obtained by one of the following processes: (1) The oldest, but the least used at the present time, consists in decomposing fused acetate of soda with sulphuric acid ( $168^{\circ}$  Tw.), then repeatedly crystallising and distilling the product so obtained, to free it from the last traces of water; (2) the second process, termed Melsen's, is based on the property which neutral acetate of potash has, of combining with an equivalent of acetic acid to form a diacetate; this salt, when heated, loses the water which it contains; it melts at about  $148^{\circ}$  C. ( $298.4^{\circ}$  F.), giving off a little glacial acetic acid, and boiling at  $200^{\circ}$  C. ( $392^{\circ}$  F.) with decomposition yields glacial acetic acid. During this distillation, as the temperature increases, care must be taken not to allow this to exceed  $300^{\circ}$  C. ( $572^{\circ}$  F.), so as to avoid the formation of empyreumatic substances. Practically the potassium acetate is crushed and introduced into a still, where an excess of 85 per cent. acetic acid is added to form the diacetate; the mixture is left to stand for some time and is then distilled. The vapours disengaged are then condensed in a silver coil. The first portions, which still contain too much water to be crystallisable, and are used for the preparation of pure acetates, being collected apart; the acetic acid, which subsequently passes over, is again distilled over neutral acetate of potash, then frozen and drained. By a final rectification, the finest crystallisable (glacial) acetic acid is obtained.

*Edible Acetic Acid (Acide acétique bon goût).*—This product is obtained by means of acetate of soda and sulphuric acid  $66^{\circ}$  B. ( $168^{\circ}$  Tw.), sp. gr. 1.840. One molecule of acetate of soda and one molecule of sulphuric acid are mixed in a copper still. This proportion yields bisulphate of soda as a residue, which can easily be run out of the still without fear of overheating, if naked fire heat be used, because the mass remains liquid until all the acetic acid has distilled. The soda salt used is that from the second crystallisation, simply passed through



the centrifugal in which it is washed. The sulphuric acid is run into the acetate of soda, and it is left to digest for some hours. The distillation is conducted over a naked fire or by steam at the atmospheric pressure, or *in vacuo* (Fig. 34); the concentrated acid distils first, whilst the water retained by the bisulphate of soda does not distil until towards the end, with the last traces of acid, which are collected apart for the preparation of certain acetates or for edible purposes. However, for this latter purpose the acetic acid must be purified from the impurities which it contains, such as hydrochloric acid or sulphuric acid, empyreumatic matters, acetate of copper, etc. For that purpose it is rectified in a steam-heated still (Fig. 35), over acetate of soda or acetate of lime, to retain mineral acids, or better, over red lead, which retains sulphurous acid as lead sulphate and at the same

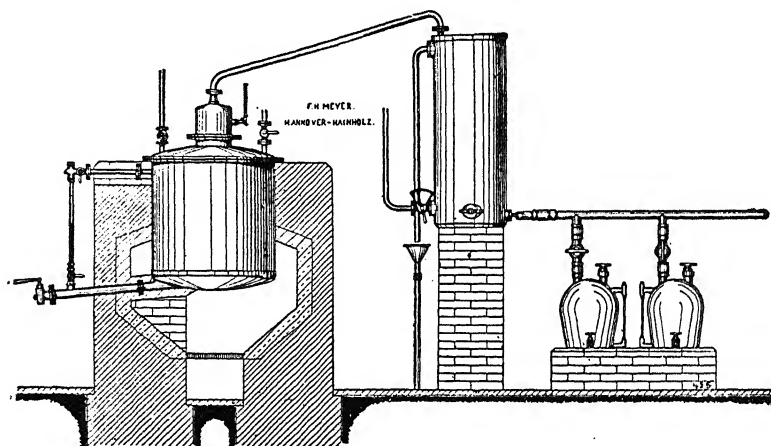


FIG. 34.—Plant for manufacturing edible acetic acid *bon goût* with distillation *in vacuo*.

time decomposes the empyreumatic matters by the oxidising action of the peroxide of lead liberated by the acetic acid. The first products, collected in a silver condenser, being very weak, are reserved for culinary uses; the strong acid which comes over afterwards is used in the preparation of the crystallisable acid. To correct the peculiar taste which acetic acid always retains, a small quantity of alcohol is added to that intended for edible purposes. The alcohol gradually etherifies yielding ethyl acetate, the agreeable odour of which communicates a flavour to the acetic acid which causes it to resemble ordinary vinegar. Finally, when it is desired to produce a product quite exempt from foreign taste, which should be the case in the preparation of table vinegar, the Mollerat process of preparing acetic acid by the cold method is used.

*Mollerat's Process.*—One part of sulphuric acid is mixed with three parts of acetate of soda (in small white crystals obtained by crystallisation in motion) in a wooden vat fitted with a perforated false bottom and a wooden agitator. The mass is then allowed to stand for twelve hours, so as to allow the sulphuric acid sufficient time to entirely replace the acetic acid. The sulphate of soda, owing to its slight solubility in the cold, crystallises on the false bottom. The acetic acid is then separated by running it out through a tap below the false bottom, and when the sulphate of soda is well drained, it is mixed with a little water; afterwards a fresh quantity of acetic acid is drawn off, contain-

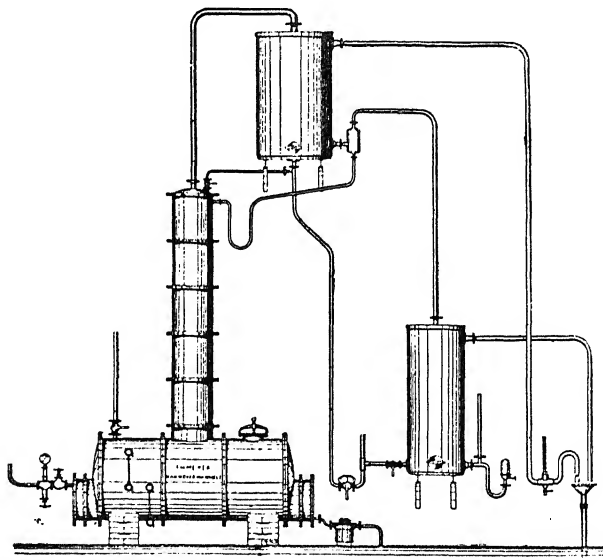
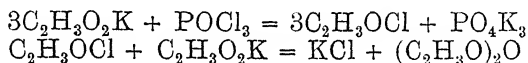


FIG. 35.—Plant for the manufacture of commercial acetic acid and chemically pure acetic acid.

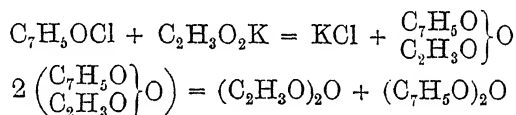
ing a little more sodium sulphate than the first, to which it is added. The acetic acid obtained is separated from the greater part of the sulphate of soda which it contains, by placing it to cool for eight to ten days in earthenware pots of 50 litres (11 gallons) capacity, arranged in a tank round which water as cold as possible circulates. The acid is then decanted and completely purified by mixing it in a vat with a paste of pure acetate of lime, in sufficient amount to decompose the sulphate of soda which it contains; the sulphate of lime thus formed is gradually deposited. The clear acetic acid is finally drawn off and diluted to bring it to a suitable strength for consumption; it still retains traces of acetate of soda which have escaped the reaction, but that is no

inconvenience. This acetic acid replaces vinegar in all cases where the taste of that obtained by distillation cannot be masked.

*Acetic Anhydride.*—The manufacture of this product belongs rather to the laboratory. Only a sketch of the different methods of preparing it will be given. (1) *By the action of oxychloride of phosphorus on acetate of potash.*—The oxychloride is run on to the fused acetate of potash drop by drop; the reaction is very energetic, though completely effected in the cold. Acetyl chloride is first produced, which, acting on the excess of acetate of potash, yields acetic anhydride—



The acetic anhydride is distilled three or four times over acetate of potash, then the product is rectified alone, rejecting any portion which may pass over below  $137.5^\circ \text{C}$ . (2) *By the action of benzoyl chloride on acetate of potash.*—Potassium chloride and benzoyl acetate are first formed, but the latter, at the temperature at which this decomposition takes place, splits up into acetic anhydride and benzoic anhydride—



which are separated by distillation. (3) *By the action of oxychloride of carbon on acetate of soda.*—In a cast-iron cylinder, fitted with an agitator, pulverised acetate of soda is heated to about  $140^\circ \text{C}$ . ( $284^\circ \text{F}$ .) without exceeding that temperature, because acetone might be produced, then a current of oxychloride of carbon is passed over the acetate of soda; acetic anhydride is disengaged which condenses and is afterwards subjected to fractional distillation.

*Wood-Spirit. Methyl Alcohol.*—The wood-spirit, obtained after having separated it from the acetic acid in the distillation over lime, is brought to 25 to 30 alcoholometric degrees, by redistilling it in a pan heated by a coil. The vapours are liquefied in a condenser, and when the product which flows away falls below  $25^\circ \text{G.L.}$  it is run back into a phlegm reservoir until about half the volume contained in the pan has been distilled. The wood-spirit of  $25^\circ$  to  $30^\circ \text{G.L.}$  is then rectified over slaked lime, so as to bring it to  $90^\circ$  to  $95^\circ \text{G.L.}$  This product, according to its percentage of oils, is more or less miscible with water; in most cases it becomes turbid on the addition of water, because it contains neutral organic products or those which do not exhibit acid properties, the boiling-point of which is approxi-

mately that of methyl alcohol itself. This alcohol, being too impure for the great majority of commercial purposes, is re-distilled, so as to obtain a methylic alcohol sufficiently pure for the purposes for which it is to be used in industry. The apparatus, still used in some factories, the description of which is adopted from Ch. Vincent's *Carbonisation des Bois en Vase Clos*, consists of three distinct parts: (1) of a copper or wrought-iron pan of 2000 to 6000 litres (440 to 1320 gallons) heated on a naked fire (Fig. 36), or by a steam coil (Fig. 37). (2) Of the rectifying column, which consists of three lenticular plates (Fig. 36), or a copper receiver, in which the goose-neck terminates (Fig. 37), surmounted by six trunks of the same shape support-

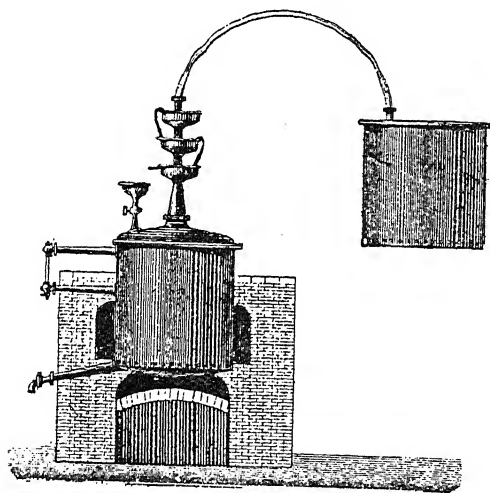


FIG. 36.—Still for the distillation by naked fire of wood-spirit for French excise purposes (*des méthylènes Régies*).

ing lenticular plates, which compel the vapours to pass along the sides of each of the trunks connected between each other by a central pipe. The top of each trunk is in the form of a basin, in which water circulates brought by a tap, the flow of which is regulated on to the top plate; the water afterwards flowing on to each of the lower plates through small pipes running from the bottom of each basin; from the bottom of the lower receiver a pipe is fixed which returns the products condensed in the rectifier to the pan. (3) Of a coil to condense the vapours issuing from the apparatus. In contact with the multiple cooling surfaces of the column, the mixture of accholic and aqueous vapours is cooled. Owing to difference in boiling-points there is a more abundant condensation of aqueous vapours

than of alcoholic vapours, which causes an increase in the alcoholic strength of the vapour, similar to what occurs in the glass column in the laboratory. In practice, the liquid condensed in the upper portion of the column, having a temperature of about  $66^{\circ}\text{C}$ . ( $150.8^{\circ}\text{F}$ .), *i.e.* approaching the boiling point of methylic alcohol, meets as it descends the current of vapour from the pan, which in its turn volatilises the alcohol condensed by the water in the top plates, whilst at the same time it reduces a corresponding amount of water to the liquid

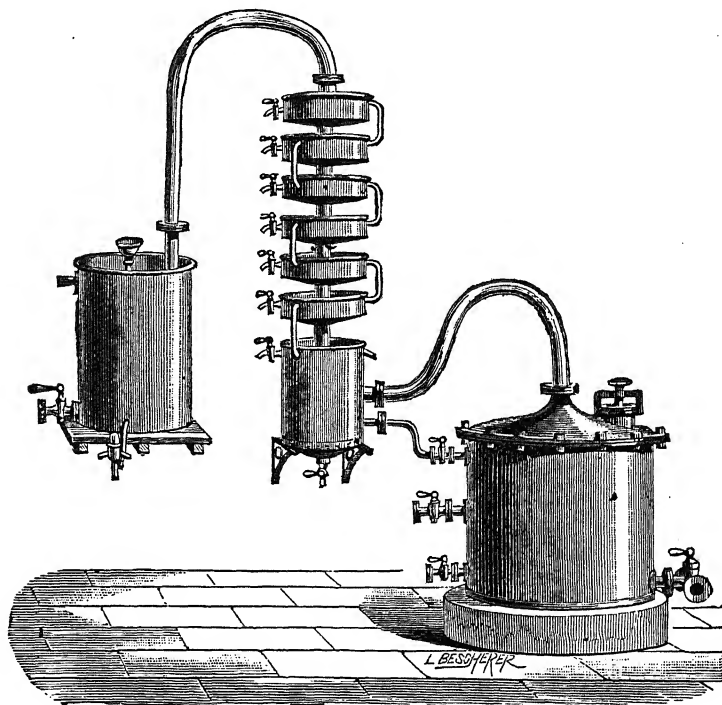


FIG. 37.—Steam-heated still for the distillation of wood-spirit.

state. It follows that with a column of six trunks of 50 cm. (19.5 inches) in diameter, 95 per cent. alcohol can be produced in one operation, starting with 30 per cent. phlegms. In addition to methyl alcohol, the product thus obtained contains acetone, ethyl aldehyde, formic aldehyde, allyl alcohol, a small quantity of methyl acetic ether (methyl acetate) which are not affected by the slaked lime and certain hydrocarbons, which cause it to become milky on addition of water. These impurities, however, are not detrimental for certain uses, such as the

denaturation of ordinary alcohol (for burning, etc.), the manufacture of spirit varnishes, etc.; but when it is to be employed for the preparation of certain aniline colours, it must be purified by a further rectification in more efficient plant, in order to free it from those hydrocarbons which, when oxidised during the course of manufacturing these dyes, would yield black products.

To purify such alcohol it is first diluted with sufficient dis-

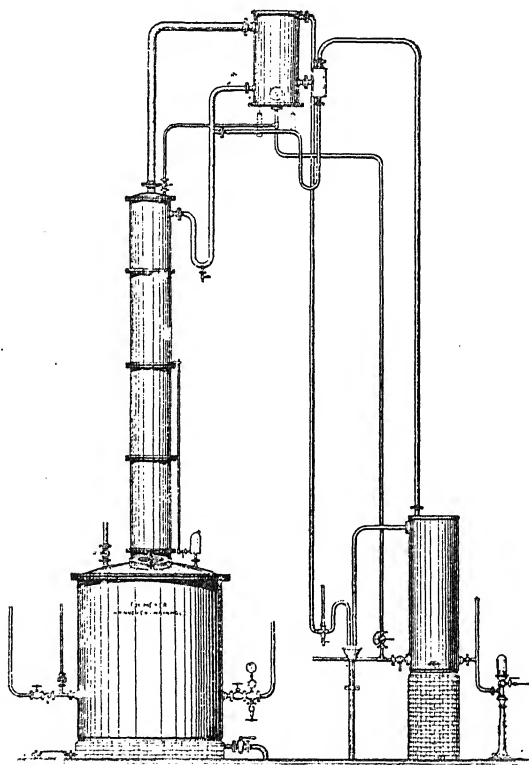


FIG. 38.—Steam-heated still for the distillation of wood-spirit, surmounted by rectification column.

tilled water to bring it to 50 per cent. strength; after standing a few days, the liquid forms two layers, the surface one of which contains the major portion of the hydrocarbons. The lower layer is then drawn off and rectified with 2 to 3 per cent. of lime in the preceding apparatus, or in a column rectifier followed by a dephlegmator, with return to the top part of the column (Fig. 38). At the commencement of the rectification every effort is made to obtain the greater part of the acetone

separately, then a slight current of water is run on to the column, which is still kept comparatively warm, and the condensed products are fractionated, collecting them in separate reservoirs, from which they are afterwards drawn off and further treated for the preparation of pure products. The condensed liquids may be divided into: (1) First runnings, testing 60 down to 8 per cent. of acetone. (2) Middle runnings, miscible with water containing 7 down to 1 per cent. of acetone. (3) Middle runnings, which do not give limpid solutions with water. (4) Portions containing allylic alcohol. (5) Last runnings, containing oils. The distilled products are tested for acetone by means of soda, by adding 20 c.c. of a solution of caustic soda of density 1.3 to 10 c.c. of alcohol contained in a graduated tube, and agitating strongly. It is then allowed to stand, when the alcohol separates entirely in a supernatant layer; this test gives no result unless the alcohol holds 1 per cent. of acetone in solution. The distillation is still followed up, testing the miscibility of the alcohol with water, and taking its strength from time to time by the alcoholometer. At the end of the operation, the distillate is no longer miscible with water; the last portions have a milky appearance, and are merely an emulsion of oil and water. The column apparatus (Fig. 38) may be advantageously replaced by a rectifier, with arrangements for the easy cleaning of the still and the column (Fig. 39), this latter not being mounted directly on the still. In spite of all the precautions which may be brought to bear in this second rectification, the methyl alcohol obtained is not yet sufficiently pure for the manufacture of methyl aniline, for example, or for the preparation of methylic ethers in the laboratory. It then undergoes a third rectification in presence of a small quantity of sulphuric acid, the distillate, between the temperatures 64° and 67° C. (147.2° to 152.6° F.), being collected for the manufacture of the above-mentioned products. Finally, when it is desired to obtain methyl alcohol free from acetone, the *Rotten* process is adopted, which consists in combining acetone with a halogen. For this purpose, methyl alcohol is distilled in a reflux condenser, into which a current of gaseous chlorine is passed, which, although inert to the alcohol, transforms the acetone into chlorinated compounds, of boiling-point about 120° C. (248° F.), *i.e.* much higher than that of methylic alcohol; the product is then distilled, after which the alcohol is rectified over lime to remove the last traces of chlorine. According to the inventor, this process yields methyl alcohol perfectly free from acetone.

*Continuous Distillation.*—Since often, for commercial reasons, it is more profitable for a wood charcoal factory to produce methyl alcohol containing small proportions of acetone

than alcohol free from acetone, a description is here given of some forms of rectification plant, in which the distillation is so much the more interesting because it is continuous, marking an important step in advance in distillery progress. Continuous rectification enables purer alcohols to be produced, whilst a considerable saving is at the same time effected.

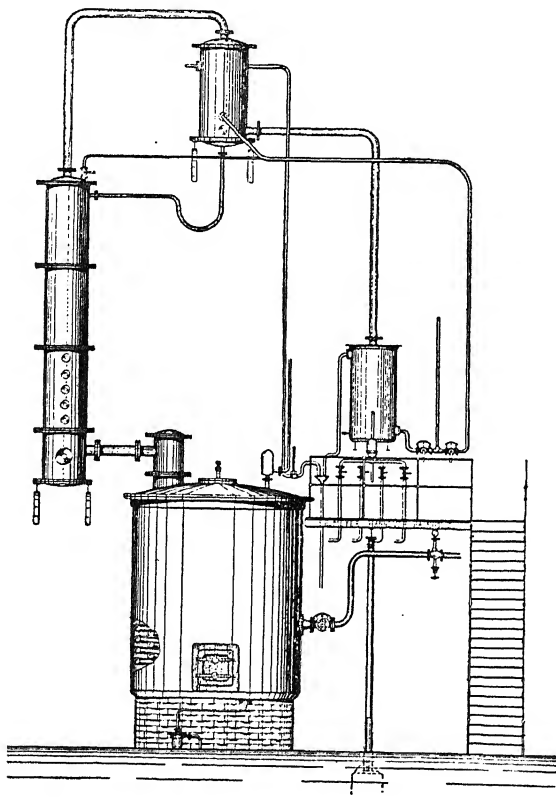


FIG. 39.—Steam-heated still, with independent rectification column, for rectification of wood-spirit.

*Coupiet's Continuous Rectifier.*—In this rectifier, the methylic alcohol vapours, after traversing a series of plates (through which they bubble) in the rectifying column, pass into three receivers, termed analysers, arranged as shown in Fig. 40, at different depths in a tank of water at a given temperature. The vapours pass into each analyser through a dipping tube in the form of a rose, and bubble into the condensed liquid, the overflow of which is brought back by independent pipes on to certain of the bubbling plates on the rectifier, making that from



the last analyser discharge at a higher level than that from the first. A tap, placed under each analyser, enables the progress of the distillation to be followed by taking samples from it from time to time.

*Barbet's Rectification System.*—In Barbet's system, the object of rectification is to make three fractional separations of the substances contained in the crude alcohol. (1) The aggregate of all which is more volatile than alcohol, or the first runnings. (2) Pure alcohol. (3) The aggregate of all which is less volatile than alcohol, or the last runnings. The crude alcohol is freed in a preliminary operation from all products more volatile than alcohol—that is *continuous purification*.

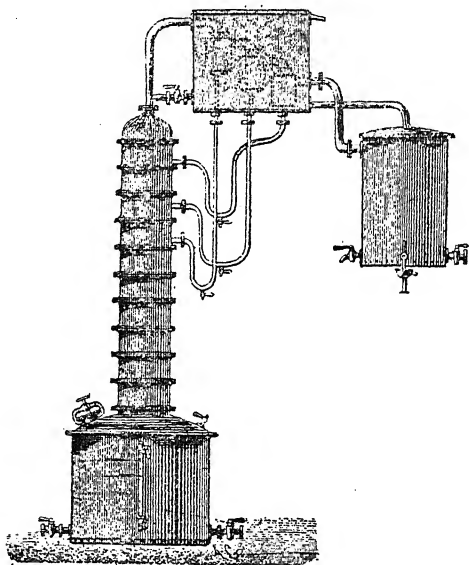


FIG. 40.—Continuous still for distillation of wood-spirit.

The purified alcohol is then delivered to the continuous rectifier properly so called, which brings it to 96 and 97 per cent. at the same time eliminating the last running's products. Barbet's continuous rectifier (Fig. 41) comprises two quite distinct parts: the purifier and the rectifier. The purifier is an ordinary distilling column A, surmounted by a small column, furnished with plates for the concentration of the ethers and to retain the pure alcohol. The alcohol, to be purified, flows into the pre-heater, R, by the pipe, S; there it is heated by the exhausted liquors issuing from the column, G. An appreciable amount of fuel is thus saved; the alcohol passes into the upper part of the column, A, in which it flows from plate to plate until it reaches

the lower part, which is heated by a coil. It is provided with a steam regulator, which is to be seen adjacent to column A. The vapours rising from the bottom of this column consist of

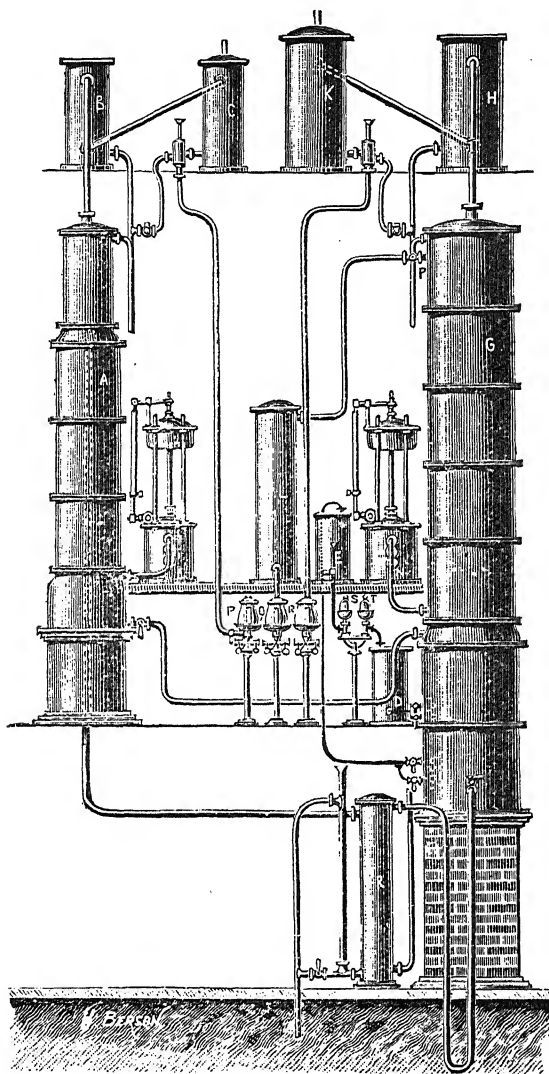


FIG. 41.—Barbet's continuous rectification plant for wood-spirit and acetone.

acetone, ethers, and alcohol; as they successively pass through the liquids lying on the plates, which become gradually less and less hot and more and more rich in acetone and in ethers, these

vapours are deprived of their alcohol, and enriched with products of lower boiling-point. These products of lower boiling-point are concentrated in the small column and pass to the condenser, B, where a retrogradation produces a methodical enrichment of these ethers and of the acetone, which are finally liquefied in the refrigerator, C, and flow out by the test glass, P.

The alcohol freed from first runnings passes by the pipe, N, into the rectifier, G, which is an ordinary distilling column, consisting of two kinds of plates: (1) exhaustion plates in the lower part, (2) rectification plates above the former. The purified alcohol, in the upper part of the exhaustion plates, descends from plate to plate and reaches the bottom of the column,

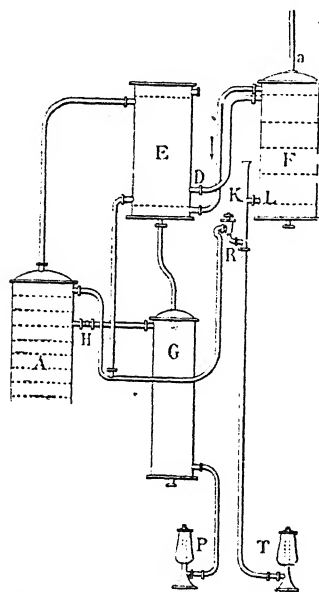


FIG. 42.—Diagram to illustrate regulation of Barbot's continuous rectifier.

which is heated by a steam coil provided with a steam regulator. During this passage it is deprived of all its alcohol; the exhausted water flowing away by the siphon, passes through the forewarmer, R, where it cedes a portion of its heat to the crude alcohol to be purified and then runs down the drain. The alcoholic vapours become stronger and stronger as they traverse the rectification plates. They reach the condenser, H, where a retrogradation sends back those vapours which condense there to the upper part of the column, G. The pure alcoholic vapours, which traverse and wash themselves in the condenser, H, pass to the refrigerator, K, the resultant liquid, that is to say, pure alcohol, flowing out through the test glass, Q. The

segregation of the products is effected on the plates in the order of their purity, the only function of the condenser, H, being to provide a wash water in which the alcoholic vapour refines itself. Thus to obtain a pure alcohol it is necessary that the washing alcohol be perfectly pure. Suppose, says Barbet, the alcohol from the test glass contains a small proportion of first runnings, the retrogradation will contain the same impurity, and will reintroduce it on to the uppermost plate of the column. But the most volatile products are re-evaporated first, and there will remain on the top plate vapours in a state of purity. The phenomenon of purification is surprisingly energetic on the top plate. The

small refrigerator, E, serves to determine the exhaustion of the residual waters; a thin stream of these waters flows constantly from the test glass, S, where they can be examined at any moment. The regulation (Fig. 42) of the flow in the continuous rectifier is rendered invariable by having the refrigerator, F, the same height as the condenser, E, and by placing them both on the same level. The cool alcohol issues by the pipe, L, fitted with an air pipe, K, and descends to the test glass, T. The alcohol drawn off from the top part of the column, A, at H is cooled in G, and flows out through P; on the descending alcohol pipe is a valve, R, connected with the retrogradation from the condenser, E. If the tap (near T) be closed whilst the apparatus is at work, the alcohol will ascend in the tube, KN, raise the valve, R, and mix with the retrogradation to enter the rectifier, A (at top). Without perturbation of any sort, without requiring more water than formerly, the apparatus continues to rectify at the same rate even though there is no outflow of alcohol. By opening the tap, N, more or less, the tap, H, being open more or less, pure alcohol is obtained. The flow of the two test glasses, P and T, can thus be regulated, and always in an invariable manner.

Lepage & Co. of Paris construct a form of rectifying still head or capital, which not only has the advantage of fitting any still, but is also economical of space, by doing away with the goose-necks and condensers of ordinary stills. The rectifying still head utilises most efficiently the condensing water, which may be replaced by the liquid to be distilled when it is desired to distil continuously. The alcoholic vapours from the pan traverse different rectifying plates contained in the chamber, C (Fig. 43). These plates, having the form of lenses with a double envelope, are cooled by a current of cold water, *r*, flowing above the funnel, E, regulated at will by a tap, by which the rectification, which may be suppressed at any given moment, may be varied as desired. The alcoholic vapours afterwards pass into a double coil, S, where they circulate in an inverse direction to a current of cold water brought by the pipe, D; the outflow of the hot water, *s*, having done duty in the rectification rejoins that (*s'*) from the condensation by the pipe, F, for their common discharge. In continuous distillation without the aid of water the liquid to be distilled first passes through the condensing coil (Fig. 44), then on to the rectifying plates. The liquid, after having been distilled in the column, falls exhausted into the pan, the residue from which is evacuated by a siphon, I. The alcohol flows from the test glass, E, at a constantly uniform strength determined by the feed tap, R.

MM. Egrot and Grange of Paris have kindly supplied the

following description of Guillaume's continuous rectification plant:—

*Continuous Rectifier for Rectifying Wood-Spirit.*—The continuous rectifier, on Guillaume's system, shown in Fig. 45, used for wood-spirit, is a modification of that used for ethylic alcohol (grain, etc., alcohol). In this apparatus the products are separated in a regular manner. The difficulty of separating the pure products from the impurities will be appreciated, from

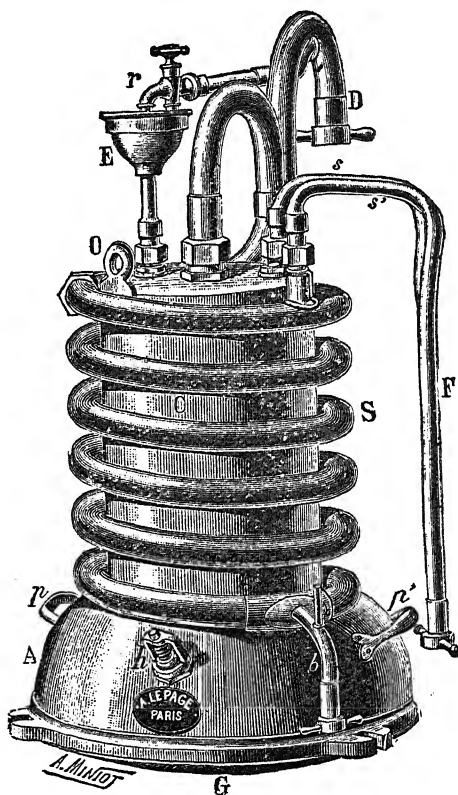


FIG. 43.—Rectifying still head.

the fact that it is necessary to vary the quantities extracted according to the impurities present in the liquids to be rectified. The efforts of Guillaume have been directed towards obtaining the necessary regularity by fitting the apparatus with a "fly-wheel" to cope with slight fluctuations. The following description explains how Guillaume has secured the remarkable results to which the adoption of this apparatus is due. The plant, as a whole, consists of a purifying column BB', in which the most

volatile portions are removed; the alcohol then passes into the concentration column, C, which is supported by a wrought-iron receiver, V, called the accumulating receiver. The last runnings are extracted in the lower part of the concentration column, and the almost pure alcohol is extracted from the top of

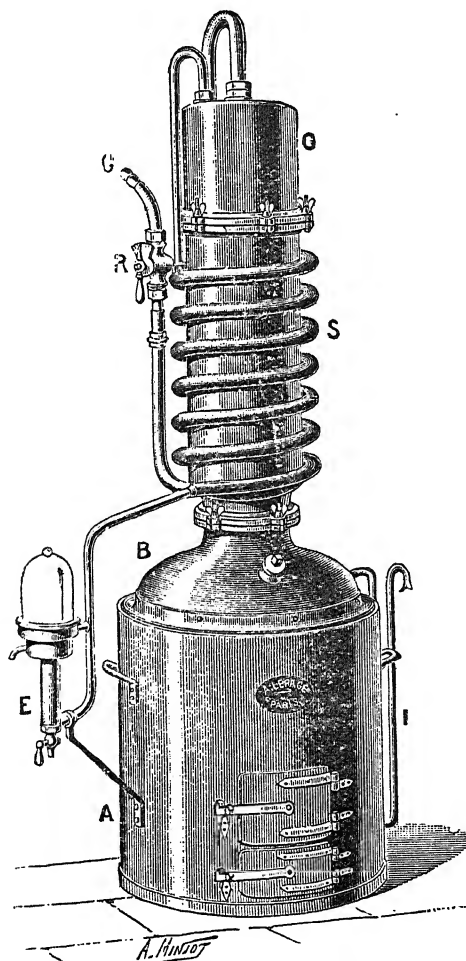


FIG. 44.—Lepage's rectifier for continuous distillation.

the rectification column to undergo afterwards a further distillation in the column DD', in which the final purification is accomplished, from which the alcohol passes to the exit test glasses. The spent or exhausted phlegm issues from the concentration column passing into the exhaustion column, E, from

which it is ejected quite free from alcohol. The plates on which the concentration of the vapours and their purification are accomplished are of a peculiar design in which the liquid is made to undergo a bubbling action as many times as there are caps. These plates have considerable exhaustion capacity. The ac-

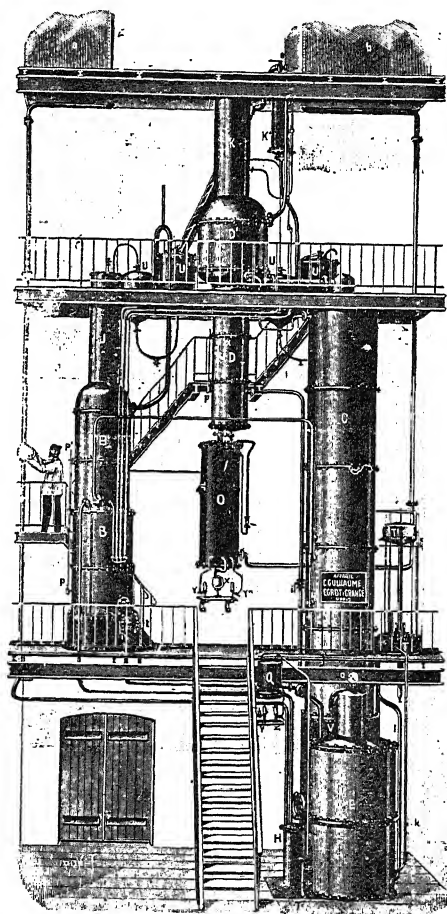


FIG. 45.—Continuous rectifier for rectifying wood-spirit.

cumulating receiver (Fig. 46) mentioned above plays an important part in the working of this apparatus. According to Guillaume, amongst the obstacles to continuous rectification which his predecessors encountered, the most important was the regulation of the apparatus, into which on the one hand there enters an alcoholic liquid, and from which on the other hand

there issue (1) the liquid from which the alcohol has been extracted, (2) the alcohol which has been separated from its impurities and collected apart. It will be readily understood how difficult it must be to adjust the apparatus, so that the pure alcohol and the impure alcohol extracted represent exactly the same quantity as that which entered therein. The delicate point is to get the alcohol issuing from the columns by the test-glass taps to balance with the alcohol introduced by the feed, without which balance the strength falls at the *bon goût* (purified alcohol) test-glass tap, or, on the other hand, a portion of the alcohol goes down the drain with the residual waters, if regulation is

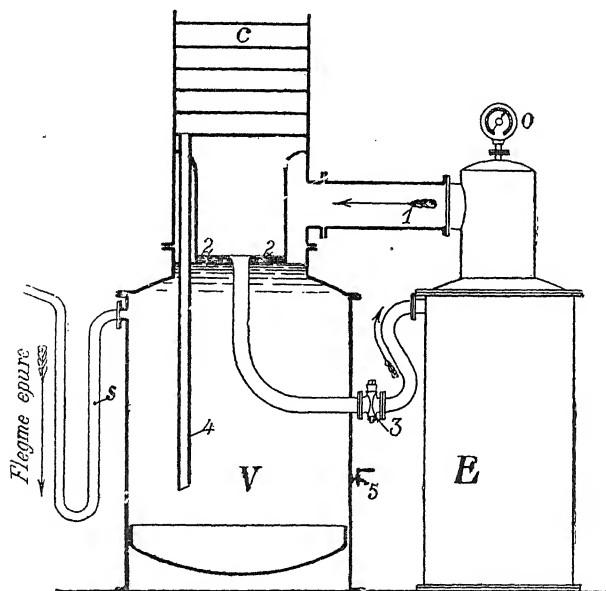


FIG. 46.—Accumulating receiver.

not perfect. The permanent supervision of the working of the rectifier does not remedy these serious drawbacks, except in a very imperfect manner. Whatever efforts be exerted, variations in the strength and purity of the rectified alcohol and loss in the spent wash cannot be avoided. The use of the accumulating receiver deals with these difficulties. This consists of a receiver, V, constantly traversed by the alcoholic liquid at a certain part of the apparatus, and is completely filled by this liquid. It forms a sort of regulating "fly-wheel" of constant volume, capable, owing to its mass, of automatically absorbing the momentary excess of alcohol which may be produced in the column without the general working being affected, and in such



a way as to place the routine working of the column under

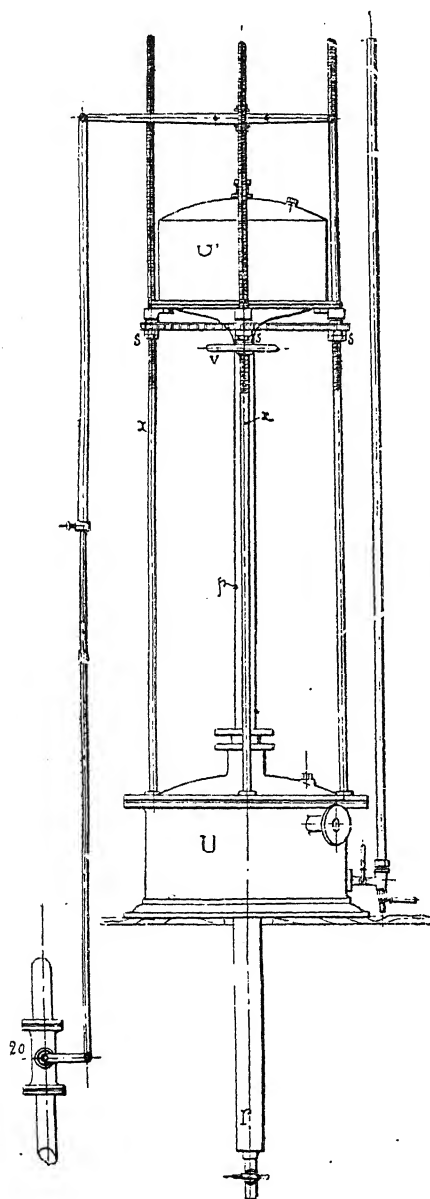


FIG. 47.—Steam regulator.

stable equilibrium. At the spot where this accumulating receiver acts the alcoholic liquid may very well vary more or less in strength by  $10^{\circ}$  or even  $20^{\circ}$  G.L., without causing any perceptible repercussion, neither on the plates above nor on the exhaustion, and without any appreciable disturbance of the separation on the plates. By having this receiver, for instance, of a capacity of 20 hectolitres it will absorb or restore 4 hectolitres of 100 per cent. alcohol for a total variation of  $20^{\circ}$  G.L. on the plate, say,  $10^{\circ}$  G.L. below or above the average degree. It will thus easily cope for four hours with either insufficient or excessive feeding, corresponding to 100 litres of 100 per cent. alcohol per hour on the flow from the test glass. This example will suffice to explain the important function which is attributed to this portion of Guillaume's apparatus. The regularity of the apparatus is still further secured by means of the automatic control of the steam and the cooling in the condensers. The regulation of the steam heating is accomplished by an adjustable regulator (Fig. 47), by which the pressure may be varied at any moment

without stopping the working of the rectifier. The consumption

of steam is greater in any given apparatus the greater the pressure at the bottom of the column; that is to say, if this pressure be increased the consumption will be greater, and, on the contrary, it will diminish if the pressure be diminished. The advantage of being easily able to regulate the working pressure so as to adapt it to the work to be done by the apparatus and to keep it as low as possible will be readily understood. If the amount of liquid to be distilled increases, the pressure is increased so that sufficient vaporisation may be produced whilst thorough exhaustion is at the same time maintained. If, on the other hand, the quantity of liquid to be distilled diminishes, the pressure is lowered so as only to consume the steam required to ensure

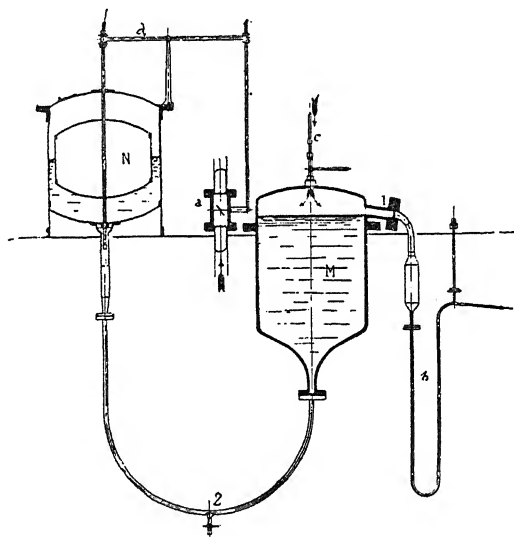


FIG. 48.—Automatic water-feed regulator.

thorough exhaustion. Fig. 47 shows this regulator in which the upper vessel is supported by screw bolts forming pinions which can be worked by means of a chain. By turning the wheel, V, these screw bolts are caused to ascend or descend together, and consequently also the upper receiver, which thus increases or diminishes at will the height comprised between the upper and lower receiver. The vertical rod which manipulates the steam distribution valve is extensible so as to adapt it to the variation in height of the upper receiver. Finally the bottom of the lower receiver has a sheath containing the plunger pipe (which slides therein) through which the liquid going to the upper receiver passes. The water feed is regulated automatically, so as to maintain a constant pressure in the condenser.

Guillaume's automatic water-feed regulator consists of two communicating vessels (Fig. 48), of which one is completely closed, and receives the pressure from the condenser. This pressure acts on the water contained in the communicating vessels; and, under its influence, the water rises into the other receiver which is open to the air, raising a float, which works the valve feeding the water into the condenser. The value of this very simple appliance is more especially enhanced by the right proportion of its parts, its good construction, and its absolutely safe working. It regulates within very narrow limits the amount of water with which to feed the condenser according to the amount of vapours to be condensed. Guillaume's apparatus works, generally, with the water tap full on, the valve of the regulator alone regulating the water feed.

*Messrs. Blair, Campbell & McLean's Plant for Wood Distillation.*—As an illustration of the most complete modern plants for the distillation of wood and the rectification of the products manufactured may be mentioned those constructed by Messrs. Blair, Campbell & McLean, Ltd., of Glasgow, who give a short description as follows:—

*Retorts.*—The retorts (Fig. 49) may be either of the horizontal or vertical type, varying in capacity from 1 to 15 tons per twenty-four hours. These are so arranged in the brick furnace settings that they are not only economical in construction but they utilise the heat so effectually that there is a saving in fuel of about 30 per cent. as compared with the ordinary types. The waste heat from the furnaces is also further economised in drying the acetate of lime.

*Condensers.*—These are an improved tubular type constructed of copper or gun-metal throughout. No choking or coking of the vapour pipes between retort and condenser is possible while the water consumption is very low (Fig. 49).

*Gas Separator.*—This is made of copper, and is attached to the condenser.

*Gas Scrubbers.*—Are of the patent tubular refrigerating type, and serve for separating the particles of tarry matter and wood alcohol which are mechanically carried over by the uncondensable gases.

*Crude Acid Stills.*—These are of the pot type for small capacities, but for large installations a patented vertical spiral continuous type is provided. This gives a dry boiled tar residue and a nearly white distilled acid, with an automatic separation of light and heavy oils and resins (Fig. 50).

*Neutralising and Sludging Apparatus.*—This is made of acid-resistant wood and bronze where in contact.

*Continuous Alcohol Distillation Plant.*—For small capacities and also for making special grades of pure or refined alcohol,

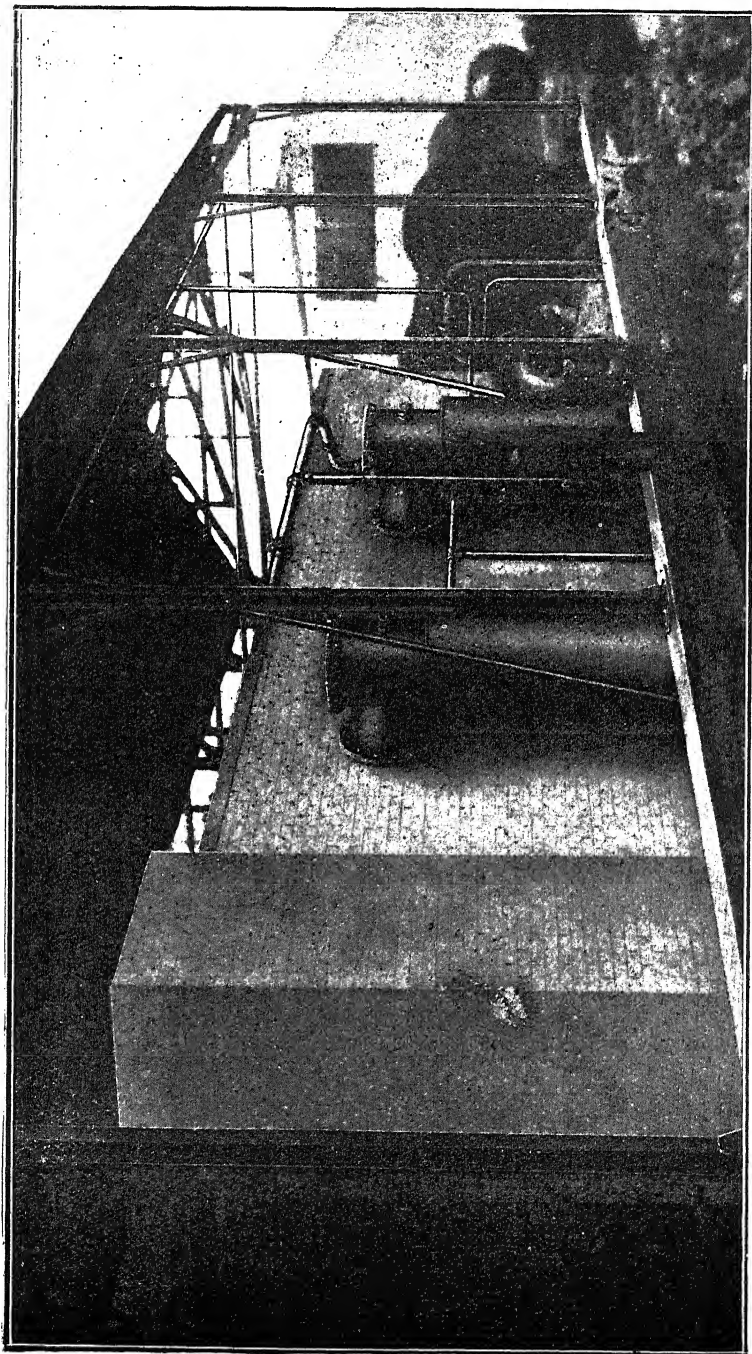


FIG. 40.—Wool distillation retort with condensers and coolers (Blair, Campbell & McLean, Ltd.).

acetone, etc., a single column discontinuous still is provided (Fig. 51).

The double column apparatus (Fig. 52) deals with the neutralised acetate liquor, producing in one operation the following liquids:—

1. Refined head products, or 20 per cent. acetone and

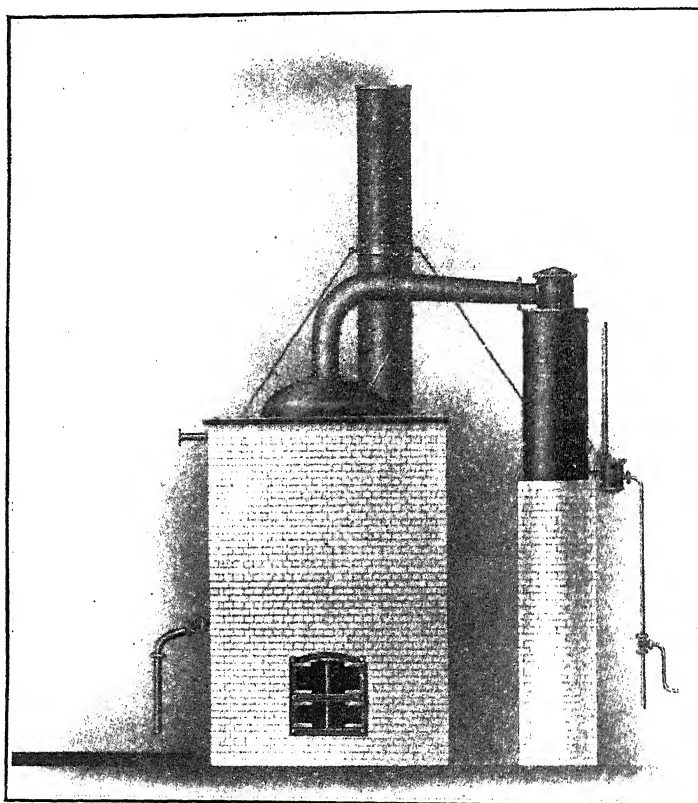


FIG. 50.—Pot type crude acid still (Blair, Campbell & McLean, Ltd.).

aldehydes with some spirit, testing about 95° Tralles hydrometer, and colourless.

2. Partially refined wood alcohol, containing about 5 per cent. acetone and traces of wood oils, testing 95° to 97° on Tralles hydrometer.

3. Distilled tail products or wood oils.

4. Alcohol free acetate of lime solution.

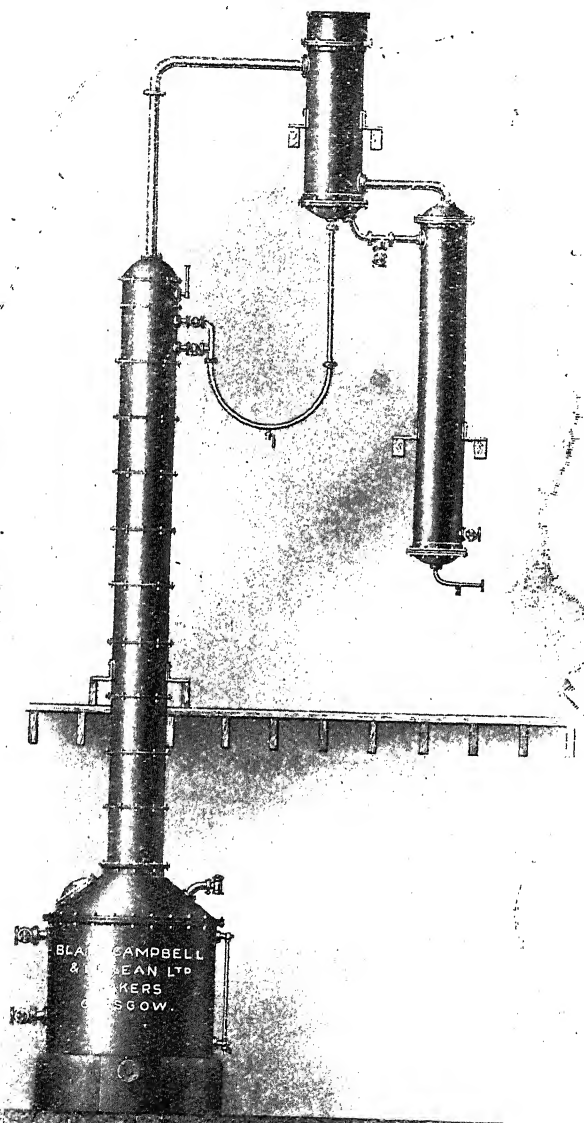


FIG. 51. - Discontinuous rectifying still (Blair, Campbell & McLean, Ltd.).

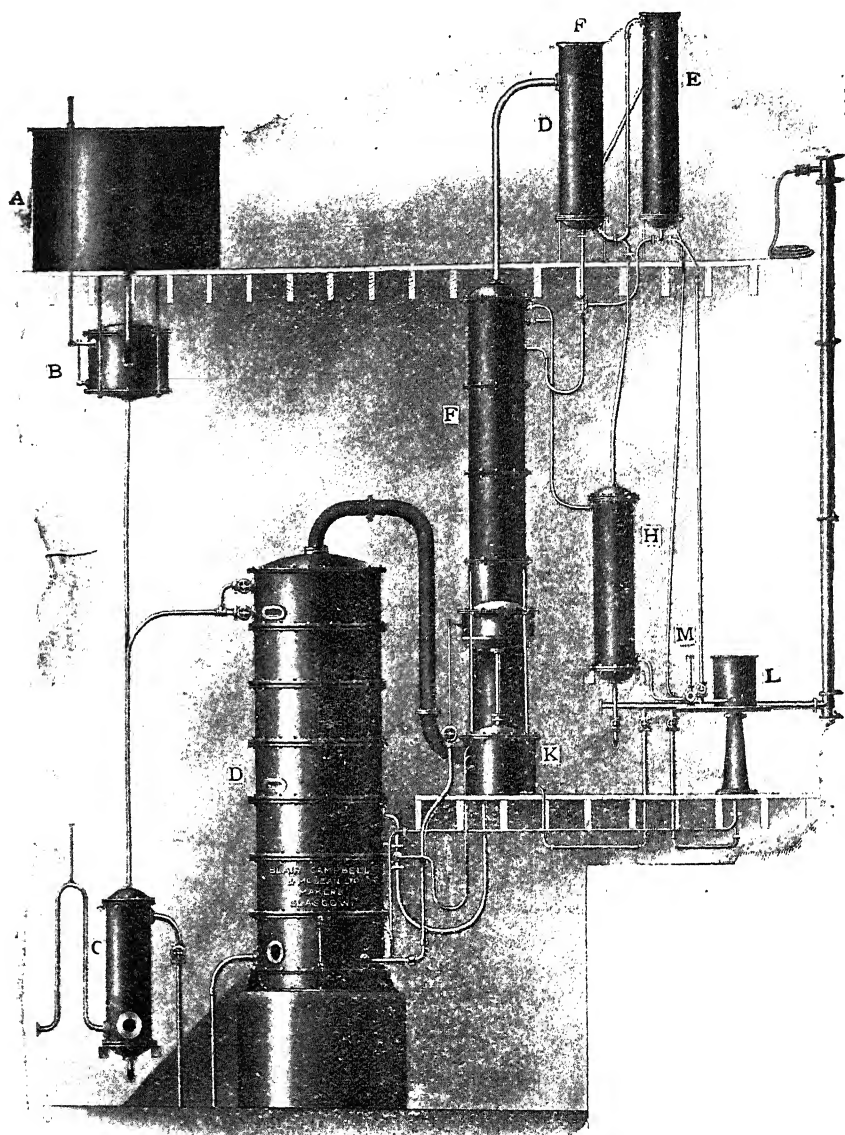


FIG. 52.—Double column continuous still (Blair, Campbell & McLean, Ltd.).

The triple column apparatus also treating crude acetate of lime liquor, yields—

1. Refined "methyl" acetone, testing 50 to 60 per cent. acetone, and 95° hydrometer, and colourless.
2. Pure refined methyl alcohol, 99·5 per cent., and colourless.
3. Wood oils.
4. Dealcoholised acetate of lime solution.

*Acetate Evaporators.*—There are two types of acetate evaporators, the single effect evaporator working under pressure. the vapours from which serve to heat the double column con-

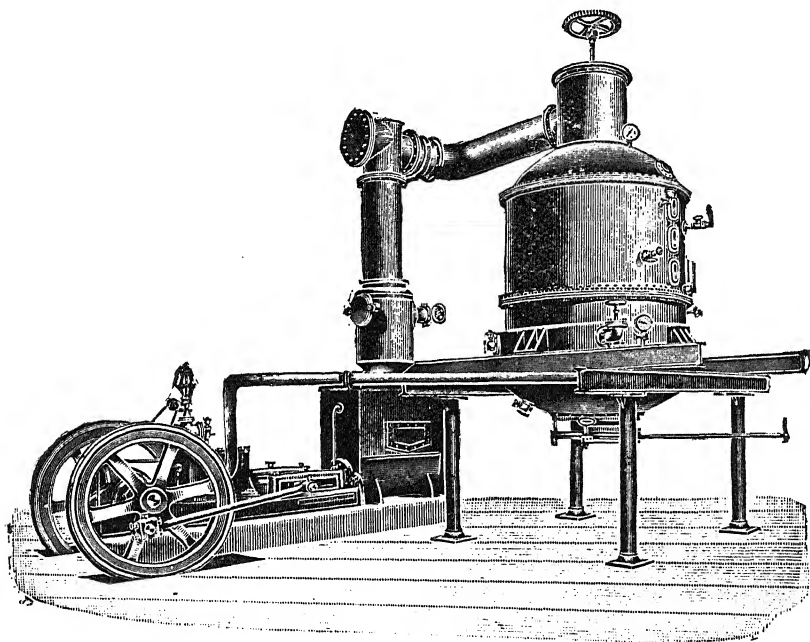


FIG. 53.—Patent vacuum evaporator single effect (Blair, Campbell & McLean, Ltd.).

tinuous still (Fig. 53). For larger installations a patent triple effect evaporator, working under vacuum, is provided (Fig. 54).

*Acetate of Lime Dryers.*—Are also of two types, the one being a steam bottom open pan fixed on top of the retort furnaces, the other of the mechanical drum type using direct steam.

*Tar Distillation Plant.*—For the distillation of tar, standard direct-fired stills are employed (Fig. 50). These serve for the preparation of creosote oil for food preservation or germicidal purposes. Plants are also provided for the rectification of the



wood tar oil and the preparation of one or more of the following:—

1. Pure medicinal wood creosote (B.P. and U.S.P.).

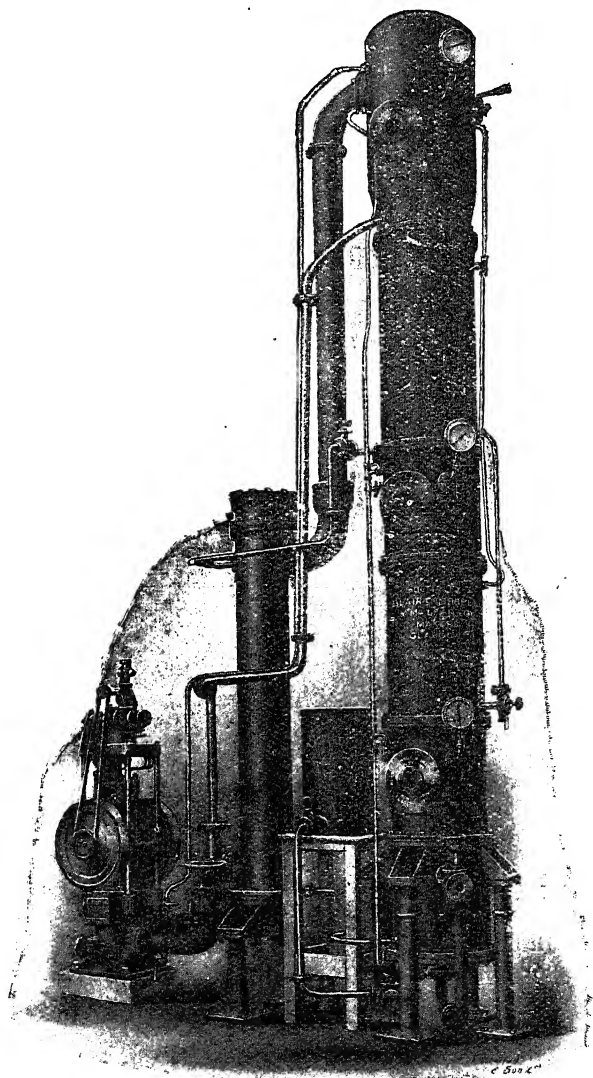


FIG. 54.—Patent "Multiplex" triple effect film evaporator (Blair, Campbell & McLean, Ltd.).

2. Officinal and commercial 20 per cent. guaiacal.
3. Refined light wood solvent oils, No 1, No. 2, and No. 3.

4. Wood creosote residual oils, No. 1, No. 2, and No. 3.

5. Hardwood pitch ("Soft," "Medium," and "Hard" grades), and recovering the acetic acid, carried in most boiled tars as acetate of lime.

In some cases, however, the tar is distilled for the production of so-called "floatation oils" which are now in great demand in the mining and metallurgical industries for the separation of valuable metallic ores from the gangue and impurities which accompany them in the natural state.

*Preparation of Pure Methyl Alcohol.*—Wood-spirit, as obtained by one of the processes given above, is not chemically pure, since it still contains 0.4 to 0.5 per cent. of acetone, aldehyde, and methyl acetate, which can only be separated with difficulty by a series of fractionations. Other methods of purification besides Rotten's must therefore be resorted to, especially in laboratories, in which advantage is taken of, at one time, the properties of methyl alcohol, at other times, of those of acetone. In one of these methods, methyl alcohol is combined with calcium chloride in powder. The crystals obtained are, after draining, heated on the water-bath to drive off the acetone and other volatile uncombined products, then they are dissolved in a certain amount of water, which decomposes the compound, and the methyl alcohol is distilled. An even better process for eliminating acetone consists in combining the latter with a freshly prepared concentrated solution of sodium bisulphite. The whole is allowed to stand while the crystals separate out; then the clear liquid is distilled. The distillate is methyl alcohol free from acetone. The acetone may be converted into chloroform or into iodoform by treating the methyl alcohol with milk of lime and a concentrated milk of chloride of lime; by afterwards submitting the liquor to distillation, the chloroform passes over first; it is collected under water so as not to lose methyl alcohol (the waters are used up in the manufacture), then, as soon as pure methyl alcohol distils, it is collected apart.

#### PREPARATION AND PROPERTIES OF THE ACETATES. DIFFERENT USES OF THESE SALTS

*Neutral Acetate of Potash.*—This salt ( $\text{KC}_2\text{H}_3\text{O}_2$ ) is prepared by directly neutralising a solution of potassium hydrate or of potassium carbonate with acetic acid. The solution, evaporated to about  $37^\circ \text{B.}$ , sp. gr. 1.345, is set to crystallise in wooden tanks lined with lead; the crystals obtained, silky and deliquescent, are then centrifuged to separate the mother liquors. The aqueous solution of acetate of potash, evaporated to dryness, is transformed into a lamellar mass with a very brilliant fracture termed

*terre folière du tartre de anciens* (*terra foliata tartari* and *febrifuge salt of Sylvius*); it melts at about 292° C., yielding foliated deliquescent crystals on cooling. It is used as an energetic dehydrating and decomposing agent. A solution evaporated with excess of acetic acid yields a crystalline mass of acid potassium acetate  $\text{KH}(\text{C}_2\text{H}_3\text{O}_2)_2$ , melting about 148° C. (298.4° F.) which is used, as already mentioned, for the manufacture of glacial acetic acid.

TABLE XIX.—GIVING THE PERCENTAGE OF ANHYDROUS ACETATE OF POTASH IN AQUEOUS SOLUTIONS OF THE SALT OF DIFFERENT DENSITIES

Densities at 15° C. (59° F.)	Potassium Acetate, per cent.	Densities at 15° C. (59° F.).	Potassium Acetate, per cent.
1.049	10	1.2105	40
1.1005	20	1.2685	50
1.1545	30	1.3285	60

*Acetate of Soda* ( $\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$ ), also termed *terra foliata mineralis* (*terre foliée minerale*).—The pyroligneous acid, separated by distillation from the methylated products, is run into wide, shallow, wooden or enamelled iron tanks, which are only two-thirds filled; Solvay soda ash is added gradually, taking care to wait a few minutes, after each fresh addition of alkali, allowing the carbonic acid to escape and the effervescence to calm down so that the liquid does not overflow. In proportion as the solution becomes less and less acid, the tarry matters held in solution, as already mentioned, by the acetic acid, separate and float on the liquid; when the liquid is neutralised, which is the case when a fresh addition of soda produces no more effervescence, the whole is allowed to stand for some time for the tars to aggregate; the latter are then skimmed off and the solution of acetate of soda is sent to the evaporation plant. If the waste heat from the charcoal furnaces is to be used for concentrating the acetate of soda, rectangular wrought-iron tanks are laid over flues, into which the furnace gases can be made to pass by means of a damper before going to the chimney. The saline solution is led into the tank the most distant from the furnace, then into the next to replace that lost by the evaporation, and so on through a series of evaporators (Figs. 55 and 56) until the liquid of the last marks 27° B., sp. gr. 1.23. At this point the damper on the flue is momentarily closed, the gases passing directly to the chimney, until the contents of the tank, brought to the right degree of concentration, are emptied into the wrought-iron crystallisers. This empty tank is now filled with the contents of the preceding one, the evaporation

being continued by bringing the furnace gases once more under the tanks. As, during this operation, tar continues to float to the surface of the mass and to soil the product, care must be taken to remove it by skimming as soon as formed. The crystallisation of acetate of soda takes several days; when it is terminated, an orifice is opened at the base of each crystalliser. The latter being slightly inclined, the mother liquors flow into a gutter which leads them to a tank at a lower level. The salt obtained in this way is placed, after draining, in a wrought-iron or cast-iron pan (Figs. 55 and 56), where the requisite amount

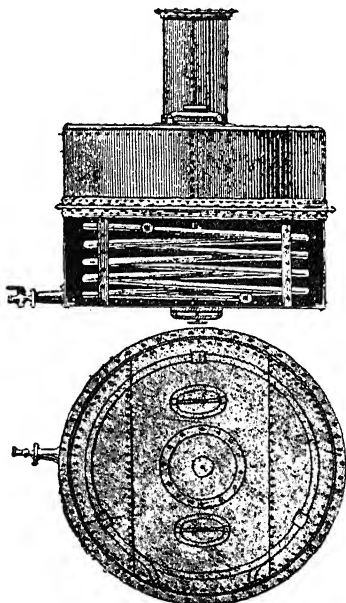


FIG. 55.—Evaporation pan for evaporating acetate of soda liquors.

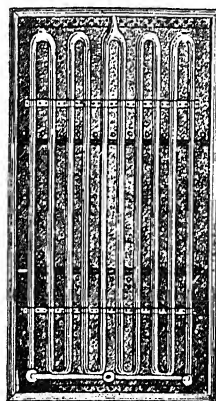
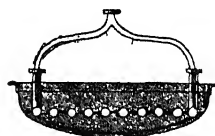


FIG. 56.—Concentration pan for acetate of soda liquors.



of water is added to make a boiling solution of 27° B., sp. gr. 1.23, which is afterwards set to crystallise in tanks. After six to ten days crystals of acetate of soda are obtained larger than the preceding, but still coloured brown; this acetate of soda of the second crystallisation may be bleached by centrifuging it and washing it in the centrifugal with a solution of purified acetate of soda. To prepare white acetate of soda, the crystals from the second crystallisation are melted, without addition of water, in a cast-iron pan, the product being then passed, in small quantities, into an adjacent pan termed the *frit*, fitted with a lid and a mechanical agitator (Fig. 57). The acetate of soda,

acetate of soda as pure as those prepared by the preceding process. This method of purifying, however, requires considerable quantities of animal charcoal.

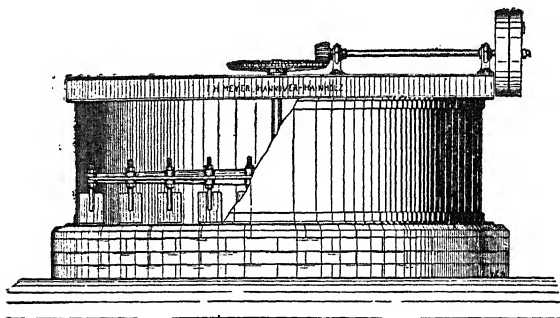


FIG. 60.—Plant for the crystallisation in motion of acetate of soda.

*Hanriot's Process.*—The solution of the first crystals is treated by tannin or crushed defibred oak or chestnut wood; the tannin precipitates the tarry matter from the liquors, which

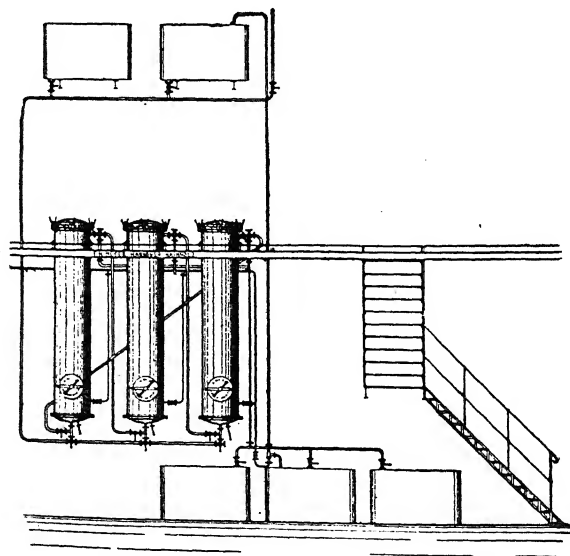


FIG. 61.—Animal charcoal filters for decolorising acetate of soda solutions.

are then separated by decantation or filtration. The solution, after evaporation and crystallisation, yields acetate of soda, suitable for the manufacture of edible acetic acid (*acide acétique bon goût*). Finally, by neutralising the acetic acid, obtained by decomposing pyrolignite of lime by a mineral acid, with Solvay

soda ash, and crystallising, white acetate of soda is obtained sufficiently pure to be used, for instance, in dyeing. Neutralisation is effected in wooden or in enamelled iron vats containing, say, 70 per cent. acetic acid, to which is added in small portions almost the theoretical amount of Solvay soda ash, bearing in mind that a small amount of acetic acid is entrained by the carbonic acid given off during the reaction. As soon as the operation is finished, the product is dissolved in water, or, better still, in the acetate of soda mother liquors from a previous crystallisation, which has been heated in a copper or cast-iron pan fitted with a lead coil. Care is taken to keep the solution slightly alkaline so that it does not act upon the metal of the pan. The acetate of soda is run into the pan in small quantities at a time so as to allow the carbonic acid remaining in the saline mass to escape without the solution overflowing. When all is dissolved it is heated to the boiling point and the boiling solution is brought to a density of 27 B., sp. gr. 1.23. It is allowed to stand for several hours, then the clear portion is siphoned off and placed to crystallise in rectangular vats of 25 cm. (10 inches) deep, where a little acetic acid is added to it, whilst it is still very hot, to neutralise its slight alkalinity. After two or three days, according to the season, the crystallised acetate of soda is separated from the mother liquor, then passed through a centrifugal with direct motor, such style of driving enabling that machine to be installed in any building through which a steam pipe passes. After being centrifuged the acetate of soda is bagged up in 2 cwt. sacks and put on the market. Acetate of soda ( $\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$ ) is efflorescent in dry air; it melts in its water of crystallisation, which it gradually and then completely loses as it is heated up to  $319^\circ\text{C}$ . ( $606.2^\circ\text{F}$ ).

*Acetate of Ammonia.*—This salt is prepared by passing ammonia gas through glacial acetic acid until no more is absorbed. The liquid becomes hot by the combination of the two substances, and on cooling it is converted into a crystalline mass. The aqueous solution of ammonium acetate, likewise called *Spirit of Mindererus*, can likewise be prepared by mixing ammonia with acetic acid in the proportion of about 30 parts of ammonia at  $22^\circ$  for 100 parts of acetic acid at  $40^\circ$ . This solution, heated to boiling, gives off ammonia and yields an acid salt which crystallises in needles; if the heat be continued, this is decomposed into water, ammonia, and acetic acid, and finally yields acetamide which distils.

*White Acetate of Lime.*—White acetate of lime is prepared by saturating lime with acetic acid the proportion being one part of slaked lime and three parts of 60 per cent. acetic acid. The milk of lime is prepared and added in small quantities to the

acetic acid, taking care that the temperature does not rise too high, so as to have the smallest possible loss of acetic acid. The neutralisation finished, the mass is allowed to cool, and the white mass so obtained is centrifuged. The acetate of lime is then laid to dry on enamelled iron plates heated, for example, by waste furnace gases.

TABLE XX.—SHOWING THE DENSITY OF SOLUTIONS OF ACETATE OF LIME OF VARIOUS STRENGTHS AT 15° C. (59° F.)

Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.
1.0066	1	1.0362	6	1.0527	11	1.0708	16	1.0925	21	1.1189	26
1.0132	2	1.0394	7	1.0562	12	1.0750	17	1.0996	22	1.1248	27
1.0198	3	1.0426	8	1.0597	13	1.0792	18	1.1027	23	1.1307	28
1.0264	4	1.0458	9	1.0632	14	1.0834	19	1.1078	24	1.1366	29
1.0330	5	1.0492	10	1.0666	15	1.0874	20	1.1130	25	1.1426	30

*Acetate of Alumina* (Calico Printers' Red Mordant).—A solution of this salt which does not crystallise is used as an ordinary mordant in calico printing. It is prepared as a more or less dilute solution, according to the purpose for which it is intended, either by double decomposition of a soluble acetate and an aluminium salt or by solution in acetic acid of freshly precipitated alumina. By double decomposition acetate of lead or acetate of lime is used, or even, and preferably, acetate of baryta when it is desired, using sulphate of alumina, to obtain an acetate exempt from sulphuric acid, sulphate of lead being slightly soluble in an acetate and sulphate of lime in water. Acetate of alumina having little stability, especially when hot, heat decomposing it, liberating acetic acid, should therefore be made cold. If lead acetate is chosen a solution of that salt, of 45° B. (91° Tw.), sp. gr. 1.455, is prepared, which is mixed cold with a solution of sulphate of alumina of 22° B. (36° Tw.), sp. gr. 1.180. The whole is allowed to settle and the solution of acetate of alumina is decanted. Acetate of alumina prepared from acetate of lime is made by running a solution in molecular proportion of acetate of lime—by small quantities at a time, to avoid an increase of temperature—into a corresponding quantity of solution of sulphate of alumina. After having mixed the two intimately it is allowed to stand, then decanted, and, if it be desired that this solution contain no sulphate, the operation is finished by the addition of a small quantity of acetate of baryta. Acetate of alumina suitable for dyers is prepared from alumina freshly precipitated from an aqueous solution of potash-alum, or ammonia-alum, by carbon-

ate of soda; the gelatinous alumina being dissolved in acetic acid. By adding increasing quantities of an alkaline carbonate to a solution of the normal salt, solutions of different basic acetates may be obtained. Impure solutions of acetate of alumina, prepared by precipitating an alkaline solution of an alum with lead acetate, are often met with in commerce. For preparing these 70 lb. of alum are dissolved in 5 gallons of water. Then 100 lb. of acetate of lead in fine powder are gradually added with constant stirring, the sulphate of lead which is formed being deposited. The liquor contains, besides acetate of alumina, sulphate of potash, sulphate of ammonia, or sulphate of soda, according to the nature of the alum used, and traces of sulphate of lead. The trade term applied to the different acetates and sulpho-acetates of alumina used in the industry is that of *red mordant*, because they are universally used, in dyeing and calico printing, to produce alizarine reds on cotton.

*Acetate of Iron.*—The acetate of iron used in dyeing black is made from pyroligneous acid freed from methyl alcohol and the greater part of its tar. It is poured in a boiling condition on iron turnings in wooden vats; the iron is soon attacked with disengagement of hydrogen, whilst the tars, held in solution by the free acetic acid, rise to the surface of the liquid in a thick layer which is skimmed off. After twenty-four hours the pyroligneous acid, now converted into a mixture of acetate of protoxide of iron (ferrous acetate) and of sesquioxide of iron (ferric acetate), is withdrawn; it marks 14° B. (22° Tw.), sp. gr. 1.100. As to the iron which remains in the vat, it must be taken out to revivify it. For that purpose it is piled in heaps and set on fire to burn off the tars which cover the undissolved turnings. The iron is then passed through a sieve to separate the oxide which is formed during the combustion, after which it can be used for a fresh operation.

*The acetate of protoxide of iron (ferrous acetate)*, used in making certain inks and in calico printing, is prepared by dissolving iron in acetic acid in a copper pan. To facilitate the reaction the whole is heated to about 70° to 80° C. (158° to 176° F.), then it is allowed to cool. As the oxygen of the air transforms this salt into ferric acetate it is run off into closed vessels. The presence of catechol, which acts as a reducer on the ferrous acetate, prevents it from oxidising too rapidly, a fact which enables it to be preserved. It may also be prepared by double decomposition of a solution of acetate of lime or of lead and ferrous sulphate (green vitriol).

*Ferric Acetate.*—In order to prepare ferric acetate, either a solution of ferric sulphate may be decomposed by an acetate, or the usual commercial process may be adopted of manufacturing



it by exposing iron turnings immersed in acetic acid to the prolonged action of the air. The operation, which lasts several weeks, is carried out in casks fitted with false bottoms; the liquid which flows out at the bottom is repassed through the cask from time to time over the mass being treated. Finally, when the solution marks 10° B. (15° Tw.), sp. gr. 1·075, by the hydrometer, it is concentrated over a naked fire to 15° B., sp. gr. 1·115, for delivery to purchasers.

*Zinc Acetate.*—This salt is obtained by dissolving zinc, carbonate of zinc or oxide of zinc in acetic acid. With zinc oxide a milky paste is made consisting of oxide of zinc 100 lb., water 15 gallons, which is saturated with acetic acid of 75 to 80 per cent. strength. The whole is then heated in a pan to boiling and concentrated to 32° to 33° B. (57° to 60° Tw.), sp. gr. 1·285 to 1·300. It is then allowed to settle and the clear solution set aside to crystallise. After some time the crystals, in the form of white plates, are centrifuged, to separate them from the mother liquor, and set to dry on sieves.

*Chromium Acetate.*—This salt is prepared in solution by mixing solutions of acetate of lead and chromium sulphate or chrome alum; in the latter case the solution, naturally, contains sulphate of potash. A solution so prepared is not decomposed on boiling whatever may be its dilution. In the cold there is no precipitation by caustic alkalis, alkaline carbonates, phosphates, nor silicates, but on boiling precipitation is complete. How these properties are utilised in dyeing will be mentioned later.

*Acetate of Copper (Cupric Acetate: Verdet, Crystallised Vert-de-gris).*—This salt was for a long time prepared by dissolving the basic acetate of copper in acetic acid by the aid of heat, the operation being conducted in a copper pan. After settling, the liquors were decanted and set aside to crystallise, and to facilitate the formation and deposition of crystals, rings of split wood were introduced into the liquid which became covered with them. At the present day sulphate of copper is taken as the starting-point. It is converted into acetate by means of acetate of soda, or again it may be prepared from sulphate of copper, the copper of which is precipitated as hydrated oxide and dissolved in acetic acid. In this latter process, milk of lime, in sufficient quantity to precipitate all the copper as oxide, is added to a solution of sulphate of copper in water, taking care to stir the mass well during the addition of the milk of lime; acetic acid is afterwards added, which redissolves the hydrated oxide of copper formed, then the sulphate of lime is allowed to settle and the liquid concentrated until it begins to skin, when it is set aside to crystallise. Another and more rapid method of manufacture, which is preferred to the last process, and by which

large crystals of acetate of copper can be obtained, consists in mixing solutions of sulphate of copper and acetate of soda at an average temperature of 70° to 75° C. (158° to 167° F.). In a copper pan, heated by a steam jacket or by a steam coil, containing 800 litres (176 gallons) of water, or mother liquors from a previous operation, which are thus already saturated with acetate of copper or sulphate of copper, 300 kilogrammes (660 lb.) of crystallised sulphate of copper, is gradually added with constant stirring, whilst the temperature is kept at 70° to 75° C. (158° to 167° F.). In a second vessel made of wood or cast-iron, likewise fitted with a copper coil or a lead coil, 700 litres (154 gallons) of water or mother liquors from a previous operation are heated, in which 330 kilogrammes (660 lb.) of acetate of soda is dissolved. The hot solutions are run into a wooden vat, taking care to let the two jets of liquid reach the bottom of the vat at a certain distance from each other, and as gently as possible, so as to avoid undue agitation of the mass. The running of the soda solution is regulated in such a way that the salt according to the molecular weights is always in excess over the sulphate of copper. The affinity of the acetic acid, contained in the acetate of soda, for the copper of the sulphate or the reverse is so great that the decomposition takes place somewhat rapidly. After a few hours, according to the season, the temperature of the mixture having meanwhile fallen to about 34° C. (93·2° F.), the acetate of copper crystallises when the sulphate of soda formed is near its maximum of solubility. The mother liquors are then decanted, and the acetate of copper is centrifuged. The salt obtained is dried in a stove at a moderate temperature. There is another process which also gives good results, not only as regards the quality of the product obtained, but also in regard to cost of production, manufacturing expenses being lower than by the preceding process. It also depends upon utilising the reaction between the two salts, acetate of soda and sulphate of copper, to form acetate of copper and sulphate of soda, by simply placing crystallised sulphate of copper in contact with a solution of acetate of soda. A solution of 165 kilogrammes (363 lb.) of acetate of soda in 400 litres (88 gallons) of water (or mother liquors from a previous operation) is made in an iron or wooden vessel heated as before by a steam coil to about 80° C. (176° F.). On the other hand, on a double bottom of wood or metallic wire gauze, supported by a frame at a certain height above the bottom of a vat of about 0·4 metre (15½ inches) in depth, of 500 to 600 litres capacity (110 to 132 gallons), 150 kilogrammes (330 lb.) of sulphate of copper crystals are laid so that the solution of acetate of soda, which is run on to them, covers them completely. The beck is then covered, so that its contents remain warm for twelve hours, the time required for the complete

transformation of the sulphate of copper into acetate. When the temperature of the liquid has fallen to  $34^{\circ}\text{C}$ . ( $93.2^{\circ}\text{F}$ .), the mother liquors are decanted and the acetate of copper, a portion of which has crystallised in fine crystals in the bottom of the vat, is collected, whilst the other portion remains on the double bottom. The acetate of copper formed is centrifuged and washed in the basket of the centrifugal with lukewarm water, then it is dried at a gentle heat for twenty-four to thirty-six hours and afterwards sifted, according to the requirements of customers. The lumps which remain on the sieve are crushed yielding a duller and more bluish acetate of copper. In the two processes just described, the two mother liquors are set to crystallise afresh for the sulphate of soda to separate out. After four to five days this salt is removed from the mother liquor which is then again utilised in the manufacture of acetate of copper. The crystallised sulphate of soda is redissolved, to be purified, in a pan, where it is heated with iron turnings so as to precipitate the copper, which soils the sulphate of soda; a small amount of carbonate of soda being then added to precipitate the iron. After twenty-four hours the solution is decanted at a temperature of  $30^{\circ}$  to  $35^{\circ}\text{C}$ . ( $86^{\circ}$  to  $95^{\circ}\text{F}$ .), and, as the quantity of water (or mother liquors) from the sulphate of soda is calculated so as to have a saturated solution at that temperature, the sulphate of soda is ready to crystallise; it is then caused to undergo crystallisation while the liquid is in motion (so as to obtain small crystals which are, practically chemically pure). The copper mixed with the oxide of iron is collected and is utilised in the reproduction of sulphate of copper.

*Verdigris or Dibasic Acetate of Copper.*—This salt is prepared on a commercial scale in the south of France, especially in the neighbourhood of Montpellier, by oxidising in the air plates of copper laid in the centre of the marc from grapes.

*Neutral Acetate of Lead or Salt of Saturn (Sugar of Lead).*  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .—This salt is obtained by dissolving litharge in acetic acid or by direct oxidation of lead with air in contact with acetic acid. The acetic acid used in both cases is commercial 40 per cent. acid. (1) *From litharge.*—The preparation of acetate of lead, from litharge, consists in bringing to about  $50^{\circ}\text{C}$ . ( $122^{\circ}\text{F}$ .) a known quantity of acetic acid run into a wooden or iron vat lined with lead [heating being effected by simply bubbling steam through the liquid (that is by a perforated steam pipe)], then gradually adding litharge (with constant stirring), the weight of which corresponds to three-quarters that of the acid with 40 per cent. acetic; when neutralisation is complete, which is determined by litmus paper, it is allowed to settle, after which it is decanted into a copper pan fitted with a steam coil. The clear solution is then concentrated to  $45^{\circ}$  to  $48^{\circ}\text{B}$ .

(90° to 100° Tw.), sp. gr. 1.45 to 1.500, and it is allowed to settle for a few moments, then the clear liquid is drawn off and set aside to crystallise in shallow earthenware pans. After twenty-four hours' cooling crystallisation is complete. The pans are reversed to drain off the mother liquors and the crystals centrifuged and laid aside to dry on a frame in a stove with a strong draught of air, but heated to a temperature not exceeding 35° C. (95° F.), so as not to liberate any of the acetic acid contained in the neutral acetate, a salt which is not stable at a higher temperature. Certain manufacturers have modified this process by utilising the property which litharge possesses of being much more soluble in acetate of lead than in acetic acid. The basic acetate of lead so formed is transformed into neutral acetate by adding acetic acid until the solution is neutral. Operations are commenced by running into the solution tank a third of its capacity of acetic acid of 30 per cent. strength, which is heated until it begins to boil; then by means of a sieve, litharge, to which enough water has been added to form a paste, is introduced, whilst stirring constantly and in quantity sufficient to saturate double the amount of acetic acid run into the tank, *i.e.* about equal weights of litharge and acid. That done, the liquid is brought to the boil for a few minutes with a perforated pipe bubbling steam into the liquid. The litharge dissolves rapidly and completely to form a milky solution of basic acetate, which is converted into normal acetate by adding an amount of acetic acid equal to that originally used, whilst still continuing to stir for some time longer. In this way the loss of acetic acid will be insignificant. The point at which the normal acetate is formed may be determined by Pfunott's reaction, which consists in removing a little of the lead solution from time to time, and testing with a few drops of a 5 per cent. solution of mercuric chloride until there is no precipitate. Acetic acid is therefore added until this point is reached. Finally, the clarified liquid is evaporated in lead-lined or tinned vessels up to 50° B. (106° Tw., sp. gr. 1.53). It is set aside to crystallise in earthenware crystallisers or in shallow wooden vats. In order to remove the copper which exists as oxide in the litharge, and which dissolves at the same time as the latter, sheets of lead are suspended in the concentration vats upon which the copper will precipitate. (2) *From metallic lead.*—In this process the lead is reduced to a very fine state of division; for that purpose it is first melted in a cast-iron pot, then granulated by causing it to fall into a small tub containing cold water. The lead in solidifying assumes a spongy form. This lead is placed in a wooden column with a perforated double bottom also of wood. This vat, being about 4 metres (13.12 feet) high, slightly conical, and at its lower end, say, 2 metres (6½ feet) diameter. Acetic acid,

mixed with a proportion of mother liquors from a previous operation, is run on to the lead. The liquid passes on to the upper perforated plate placed a few centimetres below the top of the vat; it is thus spread equally over the whole surface of the lead. In order to bring to the lead the oxygen necessary for its transformation into acetate, a current of air drawn by the draught of a chimney circulates in the vat between the two bottoms; the oxidation of the lead is accompanied by a disengagement of heat, which facilitates the reaction, the initial heating of the lead is, however, performed by a jet of steam injected into the vat. The liquors are repassed over the lead until they are neutralised and mark  $48^{\circ}$  to  $52^{\circ}$  B. ( $100^{\circ}$  to  $113^{\circ}$  Tw., sp. gr. 1.5 to 1.565), according to the season, the solution being at a temperature of  $60^{\circ}$  C. ( $176^{\circ}$  F.); when it has attained the desired degree of concentration it is slightly acidulated in the vat by the addition of a little acetic acid. After some hours' standing the liquid is decanted and set to crystallise in earthenware pans or in rectangular shallow wooden vats, so as to cool the liquid somewhat rapidly, crystallisation then taking place in forty-eight hours.

TABLE XXI.—SHOWING DENSITY OF SOLUTIONS OF ACETATE OF LEAD OF VARIOUS STRENGTHS AT  $15^{\circ}$  C. ( $59^{\circ}$  F.)

Density.	°B.	Per cent.	Density.	°B.	Per cent.	Density.	°B.	Per cent.	Density.	°B.	Per cent.
1.0127	2	2	1.1084	14	16	1.2211	23.1	30	1.3588	37.9	44
1.0255	3.5	4	1.1234	16	18	1.2395	27.8	32	1.3810	40	46
1.0336	4.5	6	1.1384	17.5	20	1.2578	29.5	34	1.4043	41.5	48
1.0520	7	8	1.1544	19.2	22	1.2768	31.2	36	1.4271	43.2	50
1.0654	8.7	10	1.1704	20.9	24	1.2966	32.9	38	1.4494	44.7	52
1.0796	10.5	12	1.1869	22.6	26	1.3163	34.7	40	1.4735	46.3	54
1.0939	12.0	14	1.2040	24.4	28	1.3376	36.3	42	1.4968	48.0	56

The crystals are then freed from the mother liquor by draining, after which they are passed to the centrifugal and then to the drying stove. The deposits which are formed in this process contain much carbonate of lead, arising from the carbonic acid in the air; they may be utilised by redissolving with the aid of heat in acetic acid, and utilising the solution in a subsequent operation. In the installation of an acetate of lead factory for this process, it is necessary to avoid the use of metals in the construction of the apparatus, *especially iron*, which, being very easily attacked, would introduce impurities in the final product; this would be a great drawback, especially for acetate of lead intended to be used in colour manufacture. According to the quality of the acetic acid used in this process

more or less well-defined crystals are obtained; thus, whilst with acetic acid *bon goût* the acetate of lead is obtained in large, well-defined crystals, with commercial acetic acid containing propionic acid, butyric acid, etc., the crystallisation is imperfect, resembling a cauliflower, owing to the presence of the higher homologues of acetic acid.

*Basic Acetate of Lead.*—This salt is generally met with in solution under the name of *Extract of Saturn*, rarely in the form of the dried salt. The dried basic acetate of lead is obtained by heating in a steam-jacketed copper pan 50 litres (11 gallons) of water, in which are dissolved 40 kilogrammes (88 lb.) neutral acetate of lead. To this is slowly added 10 kilogrammes (22 lb.) of litharge, and the whole brought to the boil. The evaporation of the liquid is continued until it becomes syrupy and suddenly solidifies; the stirring is continued energetically, still maintaining the heat until it is dry to the touch. Extract of Saturn is prepared in the same way, but concentration is stopped when the liquid marks 35° to 36° B. (64° to 66° Tw., sp. gr. 1·32 to 1·330). It is then allowed to settle and the clear liquid is decanted.

*Acetin.*—The acetin met with in commerce is simply a glyceryl ester; it is obtained by heating glycerin and acetic acid, mixed in the proportion of 53 parts of glycerin of 28° B. (48° Tw.), sp. gr. 1·24, and 47 parts of glacial acetic acid, on the water-bath for twelve to fifteen hours in earthenware vessels, similar to the condensers used for mineral acids. During the time the mixture is being heated, care is taken to stir it from time to time, so that the reaction may be complete. It is then cooled for a few hours and the clear portion siphoned off. This consists principally of diacetin  $C_3H_5(O \cdot C_2H_3O)_2OH$ , but contains also mono-acetin, tri-acetin, and free acetic acid.

*Different Industrial Uses of the Products obtained in the Distillation of Wood and their Derivatives.*—The examination of the different uses of the products obtained in the distillation of wood industry entering as they do only in a secondary way into the scheme under which this treatise is framed, only the principal commercial uses of the products described above will be given.

*Wood Charcoal.*—One of the chief industries in which much wood charcoal is used is that of metallurgy; in that industry advantage is taken of the properties which carbon possesses of uniting with several metals, such as iron, for the preparation of steel and cast-iron.

*Methylic Alcohol or Wood-Spirit.*—This is principally used for heating and lighting, and for the preservation of objects; it is used as a solvent for fine oils and certain hydrocarbons, principally resins and gums. Pure methylic alcohol is used for

the manufacture of coal-tar colours, like methylaniline, which is obtained by heating wood-spirit and aniline hydrochloride under pressure. Wood-spirit, containing a certain amount of acetone, is used to denature alcohol, forming methylated spirit which is intended for use in industry.

*Wood Tar.*—The navy and mercantile marine utilise considerable amounts of wood tar for caulking ships, coating ropes, sails, and masts. The tar used for caulking is mixed with soft pitch or rosin, and the product so obtained is termed naval pitch or vegetable pitch. Human and veterinary medicine, likewise, use tar in pulmonary and cutaneous affections.

*The tar obtained as a secondary product in the preparation of pyroligneous acid* is unsuited for the uses just indicated; it is generally fractionally distilled, yielding two or three groups of products which are collected apart, for use in the preparation of creosote and carbolic acid, as will be seen later.

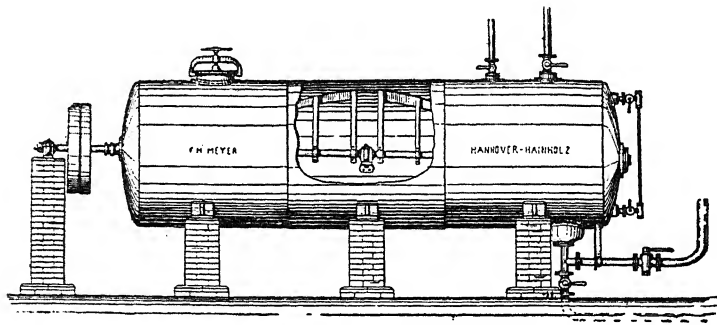


Fig. 62.—Reservoir for mixing wood-spirit.

*Acetic Acid.*—The monohydrated acid is used in photography and in chemical laboratories; under the name of *bon goût*, it is used to increase the strength of preserving vinegar, or, diluted with water, as a substitute for vinegar in cooking operations. The acetic acid of the arts serves, as already shown, for the preparation of acetates, aniline, etc. There is a great demand for it in tanning and currying for the deliming of skins, and in dyeing, as a solvent. In small amount it is used in the dye bath for tannin colours.

*Acetate of Soda.*—This salt is much used in dyeing; it is added to the nitrosamine red development baths, as well as to the printing pastes (tin salt mordants) to preserve the fibres; it is utilised as a reserve for aniline black (Prudhomme's process). For the information of the reader the preparation of a bath for nitrosamine red is given here: 4.160 kilogrammes of nitrosamine red in paste (B.A S.F.); 2 kilogrammes of hydro-

chloric acid of 20° B. (32° Tw.), sp. gr. 1.160 (30 per cent. HCl); 50 litres of water as cold as possible; in summer it will even be necessary to add a little ice; 2.800 kilogrammes of sodium acetate made up to 100 litres with water. Acetate of soda, as a white reserve for aniline black, is used in the composition of the following bath: 200 parts of acetate of soda is dissolved in 150 parts of water, then made into a paste by heating with 650 parts of British gum. For a coloured reserve use is made of 500 parts of a coloured lake of any desired colour, 150 parts of gum-tragacanth water, in which 150 parts of acetate of soda is dissolved, and 200 parts of albumen water 1 in 1. Finally, acetate of soda is used in certain dye baths with acetin.

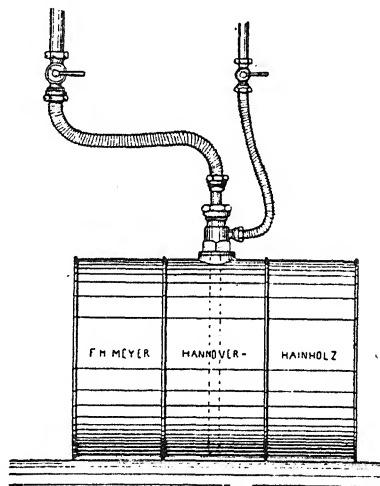


FIG. 63.—Arrangement for withdrawing the products distilled from wood-spirit from iron casks.

*Acetin*.—This product is, at the present time, utilised in large quantities in printing on cotton, because it is a remarkable solvent, both for basic colours and for colours soluble in alcohol. When steamed, the acetin facilitates the oxidation of the dyes. The following is the composition of what is termed in dyeing *un rongeant*: 350 parts of zinc dust, 350 parts of thickener, 150 parts of acetin, 150 parts of bisulphite of soda of 38° B. (72° Tw.), sp. gr. 1.360. After printing on the tissue, previously passed through the dye bath, it is dried and steamed for ten minutes under pressure, then rinsed, brightened, and rinsed once more. Acetin is employed as a salt of tin rongeant in the following proportions: First of all a hot mixture of 550 parts of acetate of tin thickener, 250 parts of acetate of tin of



21° B. (34° Tw., sp. gr. 1.17) to which are added, whilst cooling, 25 parts of tin salt, 20 parts of acetin, and 155 parts of water. Finally, by way of example, the following formula is given, into which acetin and acetate of soda enter, as rongeants, to protect the fibre: 55 per cent. of acetate of tin thickener, 20 per cent. of acetate of tin of 21° B. (34° Tw.), sp. gr. 1.170, 11 per cent. of tin salt, 4 per cent. of acetate of soda, 3 per cent. of acetin and 7 per cent. of water.

*Acetate of Ammonia.*—This compound is mostly used in medicine or for the preparation of acetamide.

*Acetate of Alumina.*—Besides its use in steam colours and in Turkey red dyeing, acetate of alumina is used in waterproofing fabrics. The pieces are passed through flannel rolls, which moisten them, with a solution of gelatine and acetate of alumina, then on drying rolls; the acetic acid of the acetate passes off while the alumina remains on the fibre.

*Acetates of Iron.*—These are much used in ink manufacture, the staining of wood black, and calico printing. Pyrolignite of iron is the mordant most frequently used in calico printing for dyeing black, violets, grenats, etc.; it is likewise largely used for dyeing silk black or for weighting raw silk. Finally, as the aceto-nitrate of peroxide of iron, it is utilised for black dyeing the silk intended for making the plush or "nap" of hats; this iron compound is prepared by dissolving iron turnings in nitric acid, until a pasty mass of basic nitrate of peroxide of iron is formed. This precipitate is collected and dissolved in acetic acid by the aid of heat, taking care to preserve a slight excess of precipitate.

*Chromium Acetate.*—The acetate of chromium in solution is used as a mordant in dyeing cotton. Cellulose possesses the property of attracting sesquioxide of chromium, by a simple immersion of several hours in an alkaline solution of acetate of chromium, which is prepared with 100 parts of chromium acetate (of density 1.115, 23° Tw.), and 100 parts of caustic soda (density 1.33, 66° Tw.), and 50 parts of water.

*Acetates of Copper.*—The acetates of copper were at one time used, as green colours, in oil painting; they enter likewise into the composition of certain mordants for dyeing black on wool. Acetate of copper is used to make a liquor, termed *vert d'eau* or *vert préparé*, which is used in the colouring of plans. It enters into the manufacture of stains for wall papers, artificial flowers, etc., and is used in the preparation of Schweinfurt (emerald) green, which is an aceto-arsenite of copper, and is obtained by mixing concentrated boiling solutions of acetate of copper and arsenious acid. Verdigris is used in large quantities for destroying fungoid diseases in plants.

*Acetate of Lead.*—The chief use of acetate of lead is in the

manufacture of the many shades of chrome yellow, forming the basis of more than thirty lakes derived therefrom. Some of these do not contain even as much as 10 per cent. of lead chromate. It is used in painting and in calico printing. Chrome yellow for painting is obtained by precipitating a solution of acetate of lead with an alkaline chromate. It is then met with as a powder of a fine yellow colour, the shade of which may vary according to the conditions under which the precipitation is performed. For dyeing fabrics a bath of plumbite of lime is made, by adding 15 to 25 kilogrammes (33 to 55 lb.) of acetate of lead to a milk of lime containing 20 to 30 kilogrammes (44 to 66 lb.) of lime and 500 litres (110 gallons) of water.

*Basic acetate of lead* is used for loading white silk, also in medicine as a lotion. The great defect of colours with a lead base is that they blacken when exposed to the action of sulphuretted hydrogen, and are poisonous.

## CHAPTER IV

### SECONDARY PRODUCTS OF WOOD DISTILLATION

*Industrial Derivatives of Wood: Chloroform.*—Chloroform, which, owing to its anæsthetic properties, is a very important product, is prepared by the action of chlorine on wood-spirit in presence of an alkali. The operation is conducted in a still of a capacity triple that of the volume of the liquid to be employed, on account of the secondary reactions that occur, which cause the mass to swell up and froth. From 35 to 40 parts of water at 40° C. (3½ to 4 gallons), in which 2 parts (2 lb.) of quick-lime, previously slaked, and 8 parts (8 lb.) of chloride of lime are beaten up, are heated in a still on the water-bath. There are afterwards added 1½ parts (1½ lb.) of wood-spirit of 85 per cent. strength, and the temperature of the apparatus is increased rapidly until the still head is well heated. Gas is given off which emulsifies the mass and causes it to froth. When this occurs the heat is withdrawn, either by removing the fire from underneath the water bath, or if heat be applied by a steam coil by turning off the steam, the distillation being allowed to proceed without external aid. Towards the end of the operation, heat is again applied to terminate the reaction. The process is complete when the liquid which distils has no longer the sweet taste of chloroform.

The distilled product is a mixture of chloroform, methyl alcohol, and water forming two layers in the receiver in which it is collected; the lower layer is chloroform, coloured slightly yellow by the chlorine which it holds in solution; this is decanted, washed with water to remove alcohol, and then with carbonate of potash solution. It is finally dehydrated with chloride of calcium, then rectified over concentrated sulphuric acid, which is without action on chloroform, so as to remove the disagreeable odour due to a small quantity of a peculiar chlorinated compound. The water which floats on the chloroform in the condensation of the distilled products may be used again in the preparation of fresh chloroform. Chloroform is more often made from ethyl alcohol, and Laroque and Husant state that, if from 41½ parts of alcohol 550 grammes of chloroform be obtained by the first operation, 640 grammes of that

substance will be got in the second operation by using the water distilled in the previous operation, 700 grammes in the third, and finally 730 grammes in the fourth operation. Again, chloroform may be made by distilling acetate of potash and acetone in presence of chloride of lime. Chloroform is a very mobile liquid, colourless, with a mild ethereal odour when it is pure, and a slightly sweet taste; its density is 1.48. It boils at  $60.8^{\circ}$  C. ( $141.4^{\circ}$  F.), and burns with difficulty with a reddish flame bordered with green; only slightly soluble in water, though it dissolves in sufficient quantity to impart a pleasant, sweetish taste to the liquid. It is very soluble in alcohol and in ether; its alcoholic solution, run into water, renders the latter milky, whilst pure chloroform gives no turbidity with water. Moreover, pure chloroform should give no turbidity with nitrate of silver, nor coagulate albumen; when it has undergone decomposition, it inflames the skin, and becomes poisonous, if it contains chlorine or hydrocarbon oils, arising from bad rectification.

*Methyl Nitrate* ( $\text{CH}_3\text{NO}_3$ ).—This ether of methyl alcohol is extensively used in the manufacture of methylaniline. It is prepared by introducing one part of nitrate of potash into a retort, and dropping on to it a mixture of two parts of sulphuric acid and one of methyl alcohol; the reaction occurs spontaneously without the aid of heat, a very volatile liquid distilling, which is led into a refrigerating condenser. The oily portion is afterwards washed with water, then rectified on the water-bath over a mixture of massicot ( $\text{PbO}$ ) and chloride of calcium, collecting that which passes over at  $66^{\circ}$  C. ( $150.4^{\circ}$  F.). Methyl nitrate is colourless, with a faint ethereal odour; its density is 1.1836 (Tw.) at  $22^{\circ}$  C. ( $71.6^{\circ}$  F.). It boils at  $66^{\circ}$  C. ( $150.4^{\circ}$  F.) and burns with a yellow flame. Very slightly soluble in water, but soluble in all proportions, in alcohol and in wood-spirit. Heated to  $100^{\circ}$  C. ( $212^{\circ}$  F.) with aniline, methyl nitrate is converted into methylaniline-nitrate, and this, treated with caustic soda lye, yields methylaniline, which is distilled so as to render it fit for the manufacture of methyl-rosaniline colours.

*Ethyl Acetate* (*Acetic Ether*) ( $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$ ).—Ethyl acetate is met with, naturally, in wine or in wine vinegar. It is utilised in medicine, but is employed more particularly for imparting an odour to the vinegars made from acetic acid produced by distillation. It is prepared by the action of acetic acid on alcohol, but, as etherification by an organic acid is accomplished slowly and incompletely, it is preferable to manufacture ethyl acetate by the intervention of mineral acid, like sulphuric acid, which is made to react on acetate of soda and alcohol. Small quantities of sulphuric acid and alcohol, previously mixed, are run into a retort containing crystallised sodium acetate, heat is applied; whereupon the liquid distils, and, after passing through

a condenser, is collected in a receiver. The distilled product is agitated with twice its volume of water rendered slightly alkaline, it is then allowed to settle, and the ethyl acetate floating on the surface is decanted and digested over calcium chloride before being rectified. Since chloride of calcium is soluble in acetic ether, bumping occurs in the still to such an extent as to render the operation a difficult one. It is therefore preferable, as indicated by Berthelot, to wash the crude product with a weak alkaline solution, and, after rectification, to agitate it with a saturated solution of common salt, dry over carbonate of potash, and finally rectify again. The wash waters, containing dissolved acetic ether and alcohol, which have escaped the reaction, are fractionally distilled; the liquid, containing the acetic ether and the alcohol, being collected and used in a fresh operation. Ethyl acetate, the boiling-point of which is  $74^{\circ}\text{C}$ . ( $165.2^{\circ}\text{F}$ .), is a colourless, very mobile liquid, lighter than water; it has a very pleasant ethereal odour, is slightly soluble in water, and very soluble in alcohol and ether. When perfectly dry it may be preserved indefinitely without decomposition, but in presence of moisture it gradually decomposes, regenerating alcohol and acetic acid.

*Amyl Acetate* ( $\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$ ).—The preparation of this ether is carried out in the same way as that of ethyl acetate, using acetate of soda, sulphuric acid, and amyl alcohol. The rectified product is washed with water, then set aside to dry over calcium chloride, and rectified with a little lead oxide. Berthelot advises that the crude product be washed with acetic acid, diluted with its own weight of water, so as to remove traces of amylic alcohol which separate with difficulty; it is then washed with water, dried over chloride of calcium, and finally rectified over lead oxide. Amyl acetate is a colourless liquid, boiling at  $125^{\circ}$ ; its density is 0.876; it is insoluble in water, but soluble in alcohol and ether. Its aromatic ethereal odour, recalling that of the pear, has led to its use in confectionery for flavouring purposes. It likewise enters into the composition of some perfumes, imparting to them a pleasant odour, as well as into certain extra fine petroleum products for toilet use (*pétroles de luxe*). It is also employed as a solvent for nitrocellulose in the preparation of varnishes.

*Acetone* ( $\text{CH}_3\text{OCH}_3$ ). *Acetone by the Dry Distillation of Acetate of Lime*.—Owing to the numerous applications of this product, the acetone industry is at the present day of considerable importance. Not only is an appreciable amount consumed in France for the manufacture of *Méthylène type Régie* (that is a mixture of 25 per cent. of acetone and 75 per cent. of methyl alcohol for the denaturation of alcohol for French industrial purposes), but it is also used in the manufacture of celluloid and

nitrocellulose varnishes. Great Britain, likewise, uses an important amount for the manufacture of its smokeless powders; finally it is used in the manufacture of chloroform. Acetone is produced in the dry distillation of acetates, and especially, as demonstrated by Chenevix, of acetates, the oxides of which can be reduced only with difficulty. The acetates of lime and baryta are those which yield the largest proportion. By heating acetate of lime to a certain temperature it decomposes into acetone and carbonate of lime  $(C_2H_3O_2)_2Ca = CaCO_3 + CH_3COCH_3$ ; but besides the principal reaction, secondary products are formed by the decomposition of lime salts of fatty acids, homologous with acetic acid, existing in the commercial acetate of lime together with hydrocarbons, due to the presence of tars which, when the temperature exceeds  $400^\circ C.$  ( $752^\circ F.$ ), are decomposed. Moreover, as the acetate of lime often contains an excess of lime, the latter reacts on the acetate to form methane (marsh gas),  $(CH_3CO_2)_2Ca + Ca(OH)_2 = 2CaCO_3 + 2CH_4$ . Hence a portion of the acetone, which, judged from the amount of acetic acid in the pyrolignite of lime, ought to be obtained, is lost, a loss which is added to by the decomposition of a portion of the acetone on the heated sides of the still. Care, therefore, should be taken in this manufacture to secure a uniform heat and regular but powerful agitation of the contents of the still. Theoretically, 100 lb. of pyrolignite of lime containing 80 per cent. of acetate of lime, ought to yield 39 lb. of acetone; but, practically, even with the best plant only 25 lb. is obtained which, after rectification, yields only 20 lb. of acetone per 100 lb. of acetate of lime.

*Installation of an Acetone Factory.*—As in the case of every industry in which condensers consisting of coils immersed in water are used, it is necessary to build the factory in proximity to as abundant a supply of water as possible. The reservoirs (storage tanks) for the different distilled and rectified products, are installed in such a way as will avoid danger by fire. The stills, boilers, engines, dynamos, pumps, etc., are arranged on the plan of a wood charcoal factory. As previously mentioned, the manufacture of acetone consists in distilling acetate of lime in a retort at a temperature which reaches a dull red heat. Water is added to the crude acetone, collected at the condenser, to separate the oils which float to the top; it is then rectified, which yields pure acetone, methylethyl acetone, and other acetone oils. The decomposition of acetate of lime is effected in cast-iron retorts fitted with an agitator, similar to those used in the manufacture of acetic acid by sulphuric acid (Fig. 64). About 300 kilogrammes (660 lb.) are distilled in one charge in these retorts. The heating of the retort, which some years ago was done in a bath of molten lead, so as to secure a uniform

heat, but had the defect of rapidly converting the lead into oxide of lead in contact with the air, is now done by naked fire. To avoid overheating and at the same time to secure uniform heating, the hearth, with the fire bridge, is placed at a suitable distance from the bottom of the pan, thus forming a rather large heating chamber, which avoids too great variations of temperature by irregular stoking. A dust chamber should be installed between the pan and the condenser to arrest the dust evolved, which might otherwise obstruct the condenser pipe. For a daily production of 1 ton of acetone, five retorts are required. Above the retorts is a floor on which the pyrolignite of lime is stored, from which it is fed into the retorts through a wooden hopper connecting with a channel which enters into

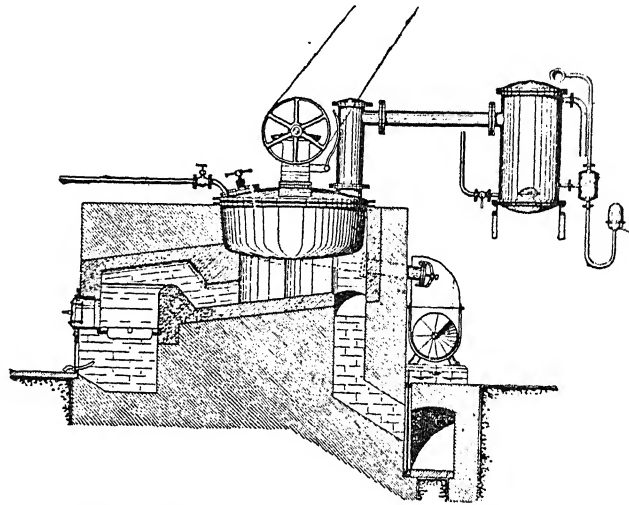


FIG. 64.—Plant for the manufacture of crude acetone.

the manhole of the retort. In small installations, the retorts are charged by emptying the sacks directly into this manhole. The pan is heated gently to a cherry red, then the acetate of lime is run in, the manhole closed and the lid luted, after which the agitator is put in motion. The vapours which are first evolved are led to the chimney, because they consist in great part of water; after some minutes distillation ceases, which necessitates an increase in the heat, to commence the decomposition of the acetate and the actual distillation of the acetone. The vapours are then led to the condenser, consisting of rectilinear pipes, connected on the outside of the tank by elbows; this arrangement enables the coil to be easily cleaned, which is necessary since it always retains entrained dust which is not

intercepted by the dust chamber. The condensed liquid has a more or less brown colour, due to the hydrocarbons which it contains and to entrainment of salts of lime in the form of dust. Towards the end of the distillation, the condensed product issues drop by drop, and the goose-neck begins to cool; when this occurs steam is injected into the retort in order to carry over a portion of the gas and dilute the remainder, so as to avoid the sudden inflammation of the gas contained in the still very hot retort when it is opened. The residue of the operation which is valueless is in the form of a fine grey powder still possessing an empyreumatic odour. The crude acetone is collected in a cast-iron cylinder fitted with an agitator; it has an average density of 0.930 and contains 30 to 60 per cent. of pure acetone. Water is added until it contains only 30 per cent. of pure acetone, then slaked lime is run in, and the liquid is stirred for some time to neutralise the free acid; it is then allowed to settle, when the solution separates into two layers: (1) A lower layer which is a dilute solution of acetone; (2) an upper and darker layer (due to the tar that it contains), consisting principally of acetone oils, the major portion of the latter being thus separated from the aqueous layer. These liquids are run into different storage tanks. The acetone liquid is then distilled in a column still, taking care to separate the first runnings, which are slightly coloured and contain aldehydes, amines, etc., from the milky last runnings, which contain the higher acetones. There are collected therefore: (1) The products which after the first runnings still contain oil, and become turbid on addition of water; (2) those which mix in all proportions with water, yet decolorise permanganate in solution; and finally (3) the most important as regards quality, product, which give no reaction with permanganate of potash and which are put on the market directly. The portions which contain the oils are agitated with water once more so as to separate them; the solution containing a little acetone being run into the crude acetone store tanks to be re-treated. To purify the fraction decolorising permanganate, the amount of this salt necessary for treating a given volume is determined in the cold state, then the corresponding weight of permanganate solution is added to the acetone, which is again rectified. In this distillation, which ought to be carried out with care, the portions of pure acetone, which pass between 56° and 58° C. (132.8° to 132.1° F.), are collected apart for use in the manufacture of chloroform and iodoform. The acetone thus prepared contains 98 to 99 per cent.

*Treatment of the Tar. Distillation of the Crude Crotonic*

The tar, separated from the crude pyrolygneous acid by decantation, as well as that precipitated in the distillation of pyrolygneous acid, forms a mixture consisting of water, saturated



hydrocarbons, both liquid and solid, such as paraffin, compounds of the aromatic series, like benzol, toluol, carbolic, and cresylic phenols as well as naphthalene. When the object is simply to free the tar from water and from light products, so as to put it on the market in that state, a copper pan, heated by a coil (Fig. 65), is used, in which the distillation is conducted with precautions to avoid priming of the tar (see also p. 83). The water distils over, bringing acetic acid, alcohol, and light oils in its train, until the distillate flows drop by drop. From 20 to 25 per cent. of distillate is collected in this way. The tar is afterwards run off from the apparatus, passing through a cooler, before storing it in barrels. The tar possesses different properties according to whether it is obtained in the partial carbonisation of

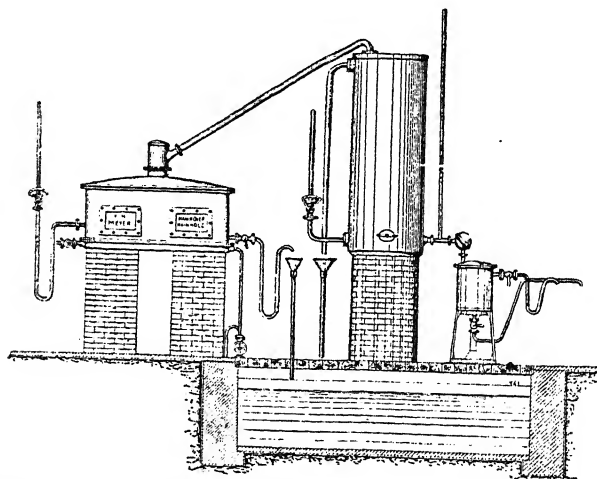


FIG. 65.—Continuous working plant heated by steam for dehydrating wood tar.

wood or from distillation in closed vessels; it varies also with the nature of the wood distilled. When it is desired to distil the tar completely, and extract the phenolic oils (or crude creosote) from it and the pitch, the crude tar is distilled in cast-iron stills similar to but smaller than those used for petroleum residues, *i.e.* 39 inches wide by 78 inches deep (Fig. 66). These stills are cylindrical, with a concave bottom; they are provided with a pipe in the bottom, with a tap for running out the pitch, protected from the action of the fire by a small masonry arch, and wide enough to obviate any stoppages in running out the pitch. Wrought-iron taps suit very well for this class of work. The lid, surmounted by a dome, the goose-neck, and the remaining plant, are generally made of copper. At the end of the condenser is a siphon, which acts as a liquid seal, and allows the uncondens-

able gases to escape to the outside, or to be aspirated by a pump and propelled to a gasometer, from which they issue through special piping, to be burned in the furnaces. The still being charged with about 1 ton of tar, the mass is heated rapidly until the copper still-head becomes lukewarm, the fire is then moderated, and the distiller, to avoid priming, waits until the first portions distilled issue from the exit of the condenser. The distilled products are collected in a separator (Fig. 67), consisting of a cast-iron case containing a vertical partition, which allows the aqueous portion to separate from the oils. All these products are fractionated into different categories, according to

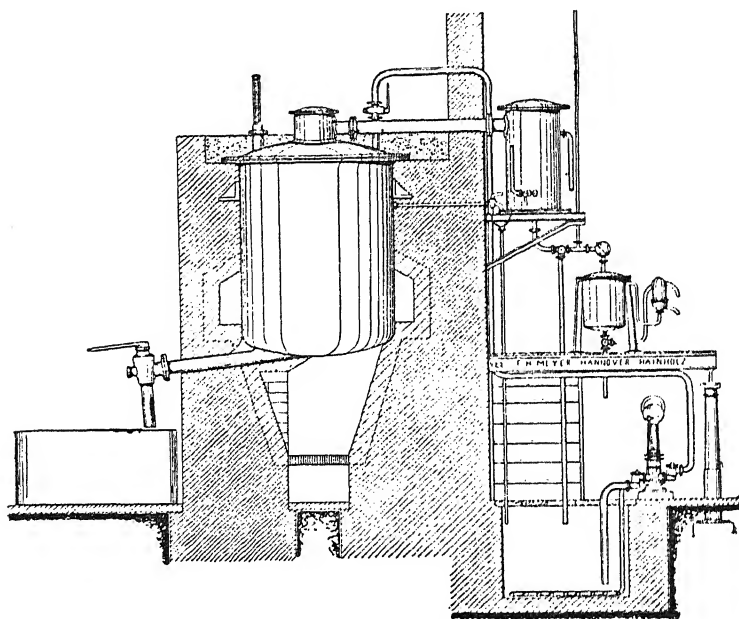


FIG. 66.—Cast-iron retort for the distillation of tar.

whether they contain both alcohol and acetic acid, acetic acid alone, or, finally, crude creosote. The distillation lasts twelve to fifteen hours according to the products which it is desired to obtain. From the quantity of tar distilled, *i.e.* one ton, there are collected on an average (*a*) between 110° and 120° C. (230° to 248° F.), from 100 to 150 litres (22 to 33 gallons) of a mixture of water, acid, alcohol, and light oils of density 0.700 to 0.800; (*b*) above 120° up to 230° C. (248° to 446° F.), from 200 to 300 litres (44 to 66 gallons) of heavy oils. These oils contain 10 to 15 per cent. of creosote, if the tar be the product of the distillation of hardwood (oak, hornbeam, beech); and 6 to 7 per cent.

only, in the case of soft woods (birch, poplar, chestnut). The residue in the retort amounting to about 6 per cent., constitutes the wood pitch, which at the temperature at the end of the distillation,  $260^{\circ}$  to  $280^{\circ}$  C. ( $500^{\circ}$  to  $536^{\circ}$  F.), is very fluid but inflammable in the air; it is allowed to cool for several hours in the still before it is discharged. The pitch is then run into extinguishers, or into petroleum barrels, sawed through the middle, which are filled directly and thus put on the market. Or the pitch may be run into a flat cooling tank, which, to prevent the product becoming kindled in the air, is covered with a wrought-iron plate, with an opening for receiving the liquid pitch; after cooling, the pitch is broken up and packed in casks. The pitch obtained by the distillation of the tar is used not only

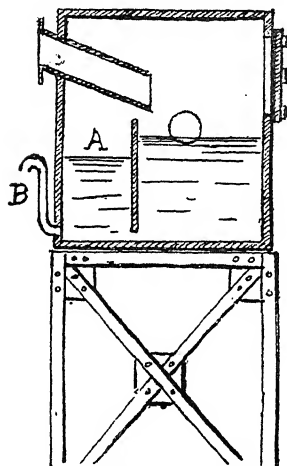


FIG. 67.—Wood-tar separator.

in making coal-blocks (briquettes), like coal-tar pitch, but it is also employed in the manufacture of artificial asphalt, certain varnishes, and coatings, and in the caulking used in the mercantile marine and navy. As to the heavy tar oils, chiefly from beech tar, these are the source of creosote and guaiacol.

*Purification of Creosote.*—Crude creosote is again distilled, to separate first the 30 per cent. of acetic acid which it still contains, then the portions passing between  $195^{\circ}$  and  $220^{\circ}$  C. ( $383^{\circ}$  to  $428^{\circ}$  F.), which constitute the phenol (carbolic acid), the cresols, and the creosol. The oil obtained being somewhat coloured, it is treated with an equal volume of a solution of caustic soda of  $36^{\circ}$  B. ( $53^{\circ}$  Tw.); sp. gr. 1.265, in a washing apparatus, with a conical bottom, bearing in the interior (Fig. 68) a helical agitator for mixing the mass and a steam coil to heat the liquid, so as to separate the greater part of the heavy oils from suspension. The phenol and the creosote combine with the soda. It is allowed to settle for some time, then the aqueous solution is decanted into a still, into which steam is injected to expel the hydrocarbons which are not capable of combining with the soda. Steam is injected into the still until a sample, taken from the interior, is limpid like water and does not turn milky on the addition of water. The solution is allowed to cool, and the oily portion which floats to the surface is again decanted, then the soda solution is treated with a mineral acid, *i.e.* hydrochloric acid or sulphuric acid, or, better still, with carbonic acid, which, in this case, is passed in at the

lower part of a column, whilst the soda solution is run in at the top. The creosote liberated in this way is fractionally distilled in copper stills with column rectifiers (Fig. 69), so as to obtain a first separation of the phenol (carbolic acid), collecting apart that which distils between  $150^{\circ}$  and  $195^{\circ}$  C. ( $302^{\circ}$  to  $383^{\circ}$  F.), then the liquid passing between  $195^{\circ}$  and  $220^{\circ}$  C. ( $383^{\circ}$  to  $428^{\circ}$  F.) which is chiefly creosote. This latter portion undergoes three different rectifications in the column apparatus. In each rectification the products passing between the temperatures indicated are collected in the same reservoirs: (a)  $195^{\circ}$  to  $205^{\circ}$  C. ( $383^{\circ}$  to  $401^{\circ}$  F.); (b)  $205^{\circ}$  to  $215^{\circ}$  C. ( $401^{\circ}$  to  $419^{\circ}$  F.); (c)  $215^{\circ}$  to  $225^{\circ}$  C. ( $419^{\circ}$  to  $437^{\circ}$  F.). This necessitates three reservoirs for

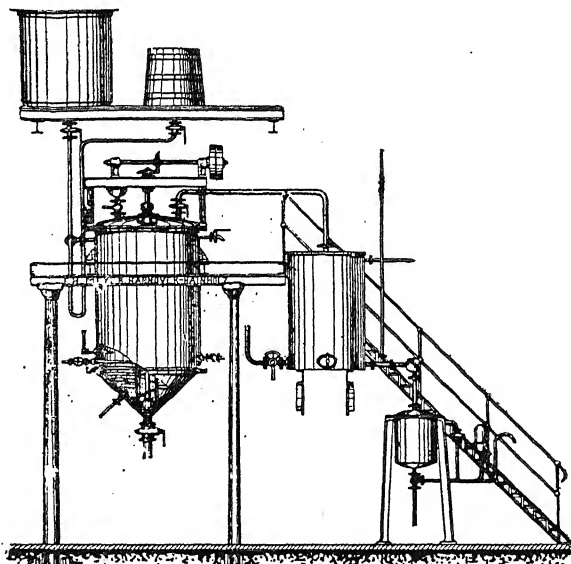


FIG. 68.—Agitator for the treatment and steam distillation of wood-tar oils.

the products of the first rectification, three others for those of the second rectification, and, finally, three other reservoirs for those of the third rectification; into these are run the products passing between the above temperatures and coming from the rectification of one of three liquids collected in the previous rectification. Finally, three fairly homogeneous liquids are obtained: (a) the products boiling between  $195^{\circ}$  and  $205^{\circ}$  C. ( $383^{\circ}$  to  $401^{\circ}$  F.) or 20 per cent. guaiacol; (b) the products collected between  $205^{\circ}$  and  $215^{\circ}$  C. ( $401^{\circ}$  to  $419^{\circ}$  F.) which constitute crude officinal 80 per cent. creosote; (c) between  $215^{\circ}$  and  $225^{\circ}$  C. ( $419^{\circ}$  to  $437^{\circ}$  F.) the creosote from the last runnings. These products, after a second combination with soda of  $36^{\circ}$  B.

(66° Tw.), sp. gr. 1.33, then a distillation in a current of steam, as already described, and finally decomposition with 50 per cent. sulphuric acid, avoiding a heating of the mass, result in the production of prime quality compounds. To obtain white creosote, the creosote previously obtained is distilled *in vacuo*; a yellow creosote is first obtained, which is rectified a second or even a third time if necessary. To prepare crystallised guaiacol the 20 per cent. guaiacol is distilled. The monophenols first pass over, the liquid collected subsequently is placed in glass vessels, in a freezing machine, where it is refrigerated. The crystals so

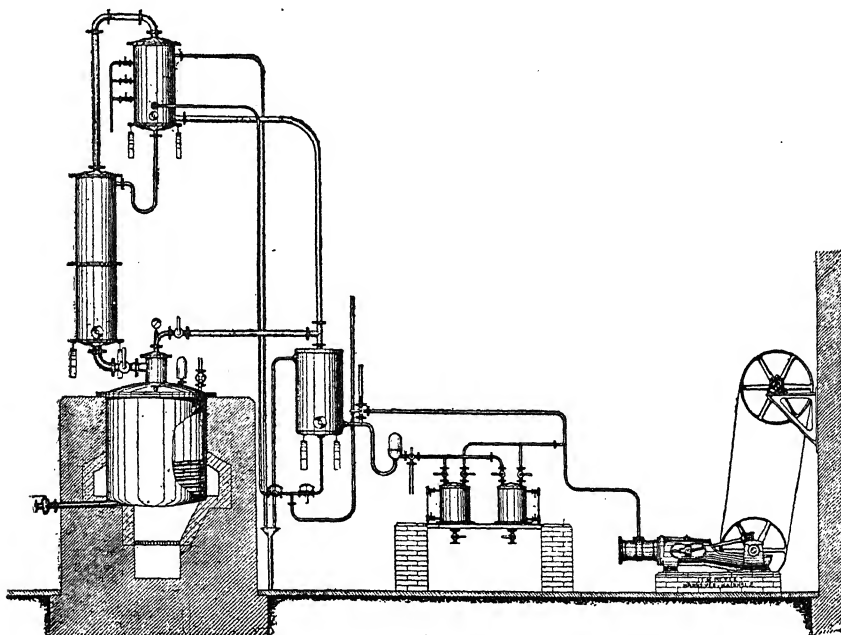


FIG. 69.—Still with column for fractionating tar oils heated by naked fire or by steam at the atmospheric pressure or *in vacuo*.

obtained are purified from mother liquor in a small enamelled centrifugal machine.

*Utilisation of Wood Waste and of Waste from Wood Charcoal Factories. Utilisation of Wood Sawdust.*—Wood sawdust, which is a cumbrous waste product in certain industries, cannot be directly used as fuel, except the ingenious furnaces with large grate surface arranged in stages are installed, but it may be otherwise profitably utilised in many ways. When a sufficient quantity is collected to warrant the erection of a first installation, it is distilled, as already described, so as to extract wood-spirit, acetic acid, and powdered charcoal. The manufacture of oxalic

acid, according to Capitaine and Herlings' process, and of glucose, and then ethyl alcohol, consume a certain quantity. Again, wood sawdust is used in the purification of gas and in the filtering of oils after purification with sulphuric acid. Finally, excellent coal blocks or briquettes are made from it, although it is somewhat difficult to get it to agglomerate, by mixing it with coal tar, glue, and an alkaline rosinate. In Austria, wood sawdust is heated until it begins to decompose, when the tarry ingredients, which it contains, separate from it; they are then ready to serve as an agglutinant. The sawdust is at once passed to the hydraulic press which moulds it into briquettes, sufficiently consistent to bear transport without crumbling.

*Manufacture of Oxalic Acid.*—Oxalic acid is produced in numerous reactions, more especially in the oxidation of organic matters. The action of nitric acid on alcohol, glycol, sugar,

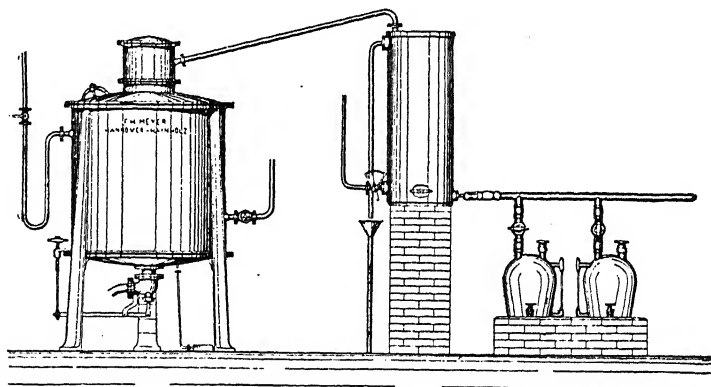


FIG. 70.—Plant for the distillation of creosote.

starch, and on cellulose yields oxalic acid. In the same way fused potash acting on sugar, starch, pectic acid and on wood sawdust produces oxalic acid. It is this latter reaction, first mentioned by Vauquelin, and later by Gay-Lussac, that is utilised commercially, at the present time, to produce oxalic acid very cheaply by the old process of Roberts, Dale & Co., of Manchester, in which many improvements have been made. The wood sawdust for this purpose is first brought to the state of paste by mixing it with an alkaline solution marking  $37^{\circ}$  to  $38^{\circ}$  B. ( $69^{\circ}$  to  $72^{\circ}$  Tw.), sp. gr. 1.345 to 1.360, consisting of potash and soda in the proportion of one equivalent of the former to two equivalents of the latter. When it is desired to make oxalate of potash, then caustic potash alone is of course used. To 100 lb. of sawdust, 300 to 350 parts of real alkali ( $R_2O$ ) are added in solution. In the beginning of this industry

the paste obtained was spread in thin layers on iron plates, which were gradually heated from beneath, care being taken to stir the mass. Now, however, this carbonisation is effected in a horizontal cylindrical retort, slightly inclined, capable of revolving on its axis, in which an archimedean screw revolves in the opposite direction. This retort being heated to dull redness, the mixture swells and intumesces during the evaporation, with generation of gases, which are burnt in the furnace. The archimedean screw, which continually moves the mixture of sawdust and alkali, conveys the carbonised material from the upper to the lower end of the retort, whence it is run into trucks which convey it to the lixiviation house, where the alkaline oxalate is extracted. For this purpose the charred mass is dissolved in a minimum of water at  $10^{\circ}$  to  $20^{\circ}$  C. ( $50^{\circ}$  to  $68^{\circ}$  F.); this dissolves the alkaline oxalates, which are more soluble in cold than in hot water. The liquid, after setting, is decanted and evaporated to dryness. The oxalates are again dissolved in cold water, the solution being brought to the boil and treated by lime to precipitate oxalic acid, and regenerate the caustic alkalis which remain in the liquid and can be utilised for a subsequent operation. The precipitate of oxalate of lime is washed with water, then decomposed by a slight excess of sulphuric acid in order to liberate oxalic acid. According to Chandelon, one molecule of oxalic acid requires three molecules of sulphuric acid, but theoretically it should need only one. The salt is rubbed up with water to a thin paste, and the requisite amount of sulphuric acid at  $15^{\circ}$  to  $20^{\circ}$  B. ( $23^{\circ}$  to  $32^{\circ}$  Tw., sp. gr. 1.115 to 1.160), is added with stirring. After adding water it is heated for a few hours, then filtered to separate the sulphate of lime. The solution of oxalic acid, after evaporation, is left to crystallise in lead vessels; but, as the crystals of oxalic acid so obtained are slightly coloured, they are purified by redissolving them in water and recrystallising. The residue, left after exhausting the carbonised mass with cold water, is calcined in a reverberatory furnace; yielding a mixture of carbonate of potash and soda, which is causticised with lime for use in a subsequent operation. From 100 lb. of wood sawdust 50 to 60 lb. of oxalic acid are obtained, and as in this process the alkalis, with but slight loss, are again used, the greatest expense is for coal, of which 40 lb. are required to make 1 lb. of oxalic acid, but the total costs are sufficiently low to enable oxalic acid to be prepared 50 per cent. cheaper than that obtained by the action of nitric acid on starch or on molasses. In Gouley's process, the sawdust is subjected to a preliminary purification by levigating it with boiling water, for extracting the tannic acid which it contains. By this method it is stated the yield is increased.

TABLE XXII.—SHOWING THE AMOUNT OF OXALIC ACID OBTAINED FROM THE SAME QUANTITY OF SAWDUST TREATED WITH MIXTURES OF POTASH AND SODA IN DIFFERENT PROPORTIONS

Ratio KHO to NaHO.	°C.	Oxalic Acid per cent.	Ratio KHO to NaHO.	°C.	Oxalic Acid per cent.
0 : 100	200-220	33.14	40 : 60	240-250	80.57
10 : 90	230	58.36	60 : 40	240-250	80.08
20 : 80	240-250	74.66	80 : 20	245	81.24
30 : 70	240-250	76.77	100 : 0	240-250	81.23

Oxalic acid crystallises with two molecules of water of crystallisation. It dries completely, but very slowly, in a dry atmosphere. It is used in very large quantities in calico printing as a resist for removal of either the mordant or the dye, so as to obtain patterns on a colourless ground. Oxalic acid is also used for dissolving Prussian blue in the manufacture of blue ink.

TABLE XXIII.—SHOWING DENSITY OF SOLUTIONS OF OXALIC ACID OF DIFFERENT STRENGTHS AT 17° C. (62.6° F.)

Density..	Per cent.	Density.	Per cent.	Density.	Per cent.
1.0035	1	1.0210	6	1.0385	11
1.0070	2	1.0245	7	1.0420	12
1.0105	3	1.0280	8	1.0455	13
1.0140	4	1.0315	9	1.0490	14
1.0175	5	1.0350	10	1.0525	15

*Manufacture of Briquettes (Coal Blocks) from Wood Charcoal.*—The waste from the carbonisation of wood, char dust, and the smalls produced in the carbonisation of twigs, have been used for many years in making small briquettes or coal blocks, sometimes termed Paris coal. In making these briquettes, glue or pitch is generally used as an agglutinant, and saltpetre to make them burn more readily. The charcoal waste is first ground and sifted and then triturated with saltpetre and a solution of strong glue or other agglutinant of 15 per cent. strength, in a circular trough by means of two conical cast-iron grooved millstones. When soft pitch or hard pitch is used to make this block fuel, the char dust, the pitch, and the saltpetre are ground in the mill, then the mixture is heated in a mixer by steam jets which penetrate into the mass, melt the pitch, and bring the paste to the right consistency for good moulding. This paste is then fed into a briquette-making machine (Fig. 71), the amount delivered to the moulds being regulated so as to obtain



hard blocks. After moulding the blocks are dried, for which purpose they are piled on trucks with shelves, which are run into a continuous drier, so arranged as to dry them gradually. The trucks enter the cooler end of a long masonry alley, which acts as a stove, and leave it by the hottest part. A current of hot air, heated to about  $70^{\circ}\text{C}$ . ( $158^{\circ}\text{F}$ .) by branched pipes, circulates in an opposite direction to the trucks. In the manufacture of Paris coal, the charcoal waste, previously moistened with 10 to 12 per cent. of water, is reduced to the state of rough powder; it is then triturated in the trough of a millstone mill, with about 10 per cent. of coal tar or molten soft pitch. Certain factories even use pulverised hard pitch. When the paste appears quite

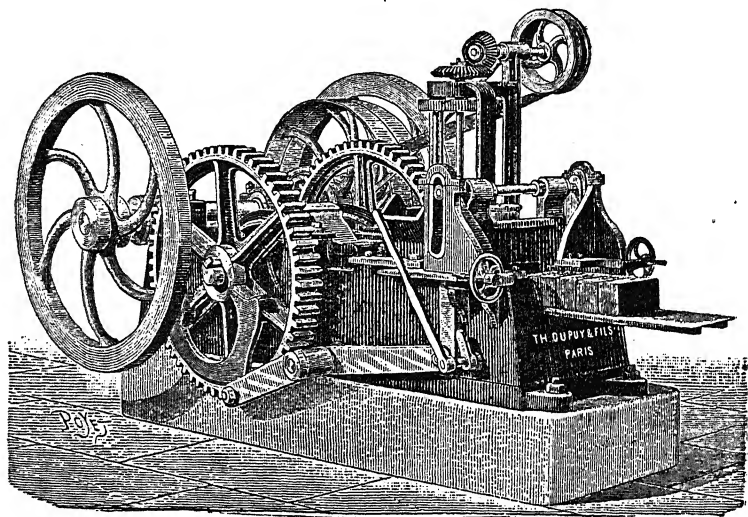


FIG. 71.—Machine for making wood charcoal briquettes or coal blocks with horizontal piston.

homogeneous, it is shovelled into a briquette-making machine (Fig. 72), from which it issues moulded into small cylinders on an endless chain, from which they are taken, to be placed in wrought-iron boxes. The boxes, full of cylinders of moulded paste, are afterwards heated in one of the muffles of a furnace, where they are carbonised; during this carbonisation the hydrocarbons of the tar are decomposed, gases are given off, which escape through holes made in the muffle, and are conducted back into the furnace, where they are utilised for the production of the heat necessary to complete the carbonisation of the coal blocks. This muffle furnace may be continuous. Carbonisation is complete when no more smoke is disengaged from the holes

made in the muffle. The contents of the muffle are run into wrought-iron extinguishers, the lids of which are luted so as to entirely avoid access of air, which would infallibly lead to combustion of the material and consequent loss; six or eight hours afterwards the extinguishing is complete, and the product is sent to the warehouse. Paris coal has the advantage, when a bright quick fire is not desired, of yielding a more easily regulated heat, and is used to a considerable extent in laboratory operations and in domestic economy.

*Manufacture of Carbonate of Potash* ( $K_2CO_3$ ).—Among the different commercial sources of which advantage is taken in the manufacture of carbonate of potash there is one, *viz.*, the ashes of plants, which falls within the scope of this treatise. The greyish residue termed ash, left on burning wood and vegetable

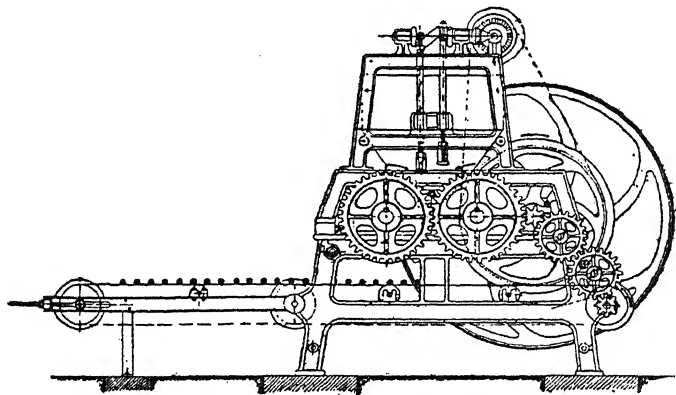


FIG. 72.—Machine for making Paris coal and briquettes for small heating appliances.

matter, contains potassium, generally as carbonate mixed with the chlorides, sulphates, phosphates, or silicates of the different alkaline bases. The carbonate of potash is separated from the other salts by systematical lixiviation. The composition of the ashes of plants varies very considerably; those which grow on the sea-shore particularly contain soda salts, whilst inland plants are especially rich in potash. As to the amount of ashes produced, it likewise varies according to the source of the plants and the nature of the soil on which they have grown. For instance, herbaceous plants leave a larger residue on ignition than ligneous plants.

The ashes contain a water-soluble portion consisting of the carbonate, sulphate, and chloride of potassium accompanied by traces of silicates, and an insoluble portion consisting more especially of carbonate of lime with a little phosphate and silica.

TABLE XXIV.—SHOWING THE AVERAGE PERCENTAGE OF ASH IN CERTAIN PLANTS

Plant.	Ash per cent.	Plant.	Ash per cent.	Plant.	Ash per cent.
Alder . . .	0.40-0.55	Oak . . .	1.80-3.3	Vine twigs . .	4.60-7.75
Hornbeam . .	0.60-1.30	Charlock . .	4.00-4.5	Pea stems . .	11.30
Pine . . .	0.80-1.10	Wheat straw .	4.50-6.3	Potato stems .	15.00

The incineration of plants, for the extraction of potash, is practised in countries where forests abound and the means of transporting wood difficult, as, for example, in certain American countries. The herbaceous plants which cover the immense steppes of Russia, and the brushwood, which is supplied by the German or by the Vosges forests, are likewise a source of carbonate of potash. The plants, dried by long exposure to air, are burnt, either in pits about 1 metre (3.28 feet) deep, or on plane, well-beaten surfaces sheltered from the wind. The combustion requires to be slow, because with too brisk a fire a part of the ash would be scorified or clinkered by the alkalis combining with the silica contained in the plants. The fire is fed until the pit is full, or until there is on the plane surface a sufficient amount of ashes. These are afterwards screened before being lixiviated. The ashes are lixiviated in casks or in vats, fitted with a perforated double bottom, the latter resting on supports which keep it about a few centimetres above the bottom, which is fitted with a bung or a lateral tube, by which the lye can be run out into a gutter, which is common to several similar casks. Generally six casks are used for the lixiviation, each alternate one being charged whilst the other is being discharged. The ashes, moistened with cold water twenty-four hours previously, are lightly packed on the perforated false bottom above a layer of straw; the addition of cold water to the dry ash not only facilitates lixiviation afterwards, but increases the yield of carbonate of potash; the silicate of potash is decomposed, under the influence of the carbonic acid of the air, into carbonate of potash and silica.

The ashes, contained in the freshly charged vat, are covered with straw and washed with a feeble lye from a vat, the exhaustion of which is nearly complete. A vertical pipe, rising from the double bottom and passing through the ashes, allows the air to escape and make room for the liquid. The vat is thus filled and started; about four hours afterwards the lye, which then contains 30 per cent. of soluble salts, is run off and evaporated. The exhaustion is stopped with the last vat, which is allowed to drain; its solid residue constitutes *charrée*, which, in

virtue of the phosphate of lime and organic matters which it contains, presents a certain value as a manure; it is also used in the manufacture of ordinary bottle glass. In France, in some factories, the old lixiviation process is still pursued; the vats used have neither false bottom nor stopcock, but in the centre of the bottom is a hole in which a central pipe, open at both ends, is fixed, and formed of several trunks, which can be separated and withdrawn as desired. The ashes, which fill two-thirds of the vat, are intimately mixed with the liquid, which is added thereto for lixiviation. They are then left to rest for some hours. The solid matters are deposited below a layer of clear liquid, which is decanted by removing from the central pipe a sufficient number of pieces; when the operation is finished, the pipe is fixed up again for a second levigation, and so on.

*Evaporation of Lyes and Calcination of the Salts.*—The lyes are evaporated in shallow, wrought-iron or cast-iron pans, into which fresh lye is being continuously added, until a sample of the liquid removed and cooled solidifies and assumes a crystalline form. At this moment the fire is moderated. A brown crystalline crust is deposited on the sides of the pan, which increases in proportion as the evaporation proceeds; when it is finished, the pan and contents are allowed to cool, and the crude dark brown potash, still containing 6 per cent. of water, is detached with a chisel. It is termed *flux*, *salin* or *potasse cassée* (crushed potash). This method of evaporation speedily wears out the pans, by the overheating to which they are exposed, when the salt adheres to the bottom (this may also cause an explosion). A better method is to stir the liquid continually with a rod as soon as it assumes a pasty condition. Drying is thus facilitated and the deposition of salt on the sides of the pan is prevented. The potash obtained in this way contains 12 per cent. of hygroscopic water and is known in commerce as *potasse brassée*. In some factories the greater part of the sulphate of potash which accompanies the carbonate of potash in the lyes is separated by taking advantage of the different solubility of the two salts. For this purpose the lyes are concentrated to the desired extent; they are then left to cool in wooden vats and are frequently stirred. The greater portion of the sulphate of potash is deposited in crystals; the supernatant solution is then decanted and evaporated as described above. In certain German factories three pans are used to evaporate the lyes. A commencement is made by heating the liquid in the first pan, that farthest from the furnace, then it is passed to the second pan, where it is brought to a syrupy consistency. Finally, the evaporation is completed on the bed of a reverberatory furnace.

*Calcination of the Crude Potash.*—The object of calcination in the air is to destroy all the organic matters which the salt

contains and which discolour it, also to eliminate the 6 per cent. of water which it contains. The operation is conducted on the bed of a reverberatory furnace, capable of taking a charge of 1·2 metric tons (24 cwt.) of crude potash, which is heated to dull redness by lateral fires, and fitted with a draught chimney in front and above the opening of the bed of the reverberatory furnace. The furnace is first brought to a red heat, then the crude potash is introduced, generally dividing the charge into tiers, and spreading it uniformly over the whole surface of the bed. The salt is stirred by a long iron rake passed through a loophole, on a level with the sole of the furnace, so as to facilitate the dehydration and promote the access of the air which burns up the organic matter. A slow fire is kept up, stirring briskly so as to prevent the mass fusing. The salt whitens gradually, and when the operation draws to a close, that is to say after about six hours' heating, a workman crushes the lumps by the aid of an iron spatula. The granulated potash is then withdrawn with the rake and is left to cool on the space in front of the furnace. Potashes so obtained are sometimes coloured red, yellow, or bluish-green, by oxide of iron or manganese. This shade is generally distinctive of its origin. The finest potash is white. It is termed pearl ash (*perlasses*, *cendres perlées*).

*Refining.*—When it is desired to extract commercial carbonate of potash from crude potashes, they are treated with an equal weight of cold water; the carbonate of potash, which is very soluble, dissolves almost alone, whilst the sulphates, chlorides, etc., remain insoluble, owing to their slight solubility, in a solution of carbonate of potash. The liquid, after decantation and evaporation, yields refined potash or commercial carbonate of potash, which, however, always contains a little carbonate of soda.

## CHAPTER V

### ANALYSIS OF RAW MATERIALS AND FINISHED PRODUCTS

THE analytical methods used in the industrial chemistry of wood, to be described in this chapter, may be divided into two sections : A. Analysis of Raw Materials; B. Analysis of Finished Products.

A. *Analysis of Raw Materials*: 1. *Lime*.—Lime is used, as already mentioned, to neutralise the pyroligneous acid; it is also used, in small quantity, in the rectification of wood-spirit. For the first purpose, which is the more important, in order to obtain the best yield, the lime should be free from magnesia, since 100 parts of acetic acid yield only 118 parts of acetate of magnesia instead of 131 parts of acetate of lime. Moreover, the lime should be almost entirely soluble in acetic acid. Consequently it should contain but little silica and silicates, which, during the preparation of the acetate, increase the amount of mud in the filter presses, and thus add very materially to the cost of washing. A large percentage of magnesia and silicates is recognised by the slowness with which the lime slakes in water: a complete quantitative analysis will determine the exact amount of impurities present in the lime. Beaumé's areometer dipped into a milk of lime containing 100 grammes of quicklime per litre (1 lb. per gallon) will give rapidly and sufficiently accurately for ordinary purposes the percentage of lime, using the table on next page.

*Quantitative Analysis*: (1) *Water*.—Ten grammes of the pulverised lime are dried at 110° C. and the loss determined.

(2) *Insoluble in Acetic Acid*.—One gramme of the pulverised lime is dissolved in acetic acid, boiled, filtered through a tared filter, the residue washed, dried, and weighed.

*Total Alkali*.—A few drops of litmus or phenol phthalein are added to the milk of lime diluted with water, and normal hydrochloric acid added until complete neutralisation is effected. 1 c.c. of hydrochloric acid = .056 gramme CaO.

*Magnesia*.—The amount of magnesia present in lime is determined by the difference in the results previously found with pure lime, estimated by Mohr's process, which consists in taking 25 c.c. of milk of lime at 2 grammes per litre, to which

25 c.c. of decinormal oxalic acid is added. Ammonia is then added drop by drop so as to render the liquid slightly alkaline; it is then boiled to precipitate the lime completely as oxalate, and after cooling the whole is run into a 200 c.c. flask, and the volume made up to the mark with water. The oxalate of lime is filtered off, 100 c.c. of the liquid is taken, 10 c.c. of concentrated sulphuric acid added, and the oxalic acid in excess is determined by titration with permanganate, from which the amount of lime can be calculated, the difference between this and the pure lime being calculated as magnesium (MgO).

TABLE XXV.—SHOWING THE PERCENTAGE OF (CaO) QUICKLIME IN MILK OF LIME OF DIFFERENT DENSITIES

°B.	Density.	Lime in 1 Litre in Grammes. <sup>1</sup>	°B.	Density.	Lime in 1 Litre in Grammes. <sup>1</sup>
1	1.007	7.5	14	1.108	187
2	1.014	16.5	15	1.116	148
3	1.022	26	16	1.125	159
4	1.029	36	17	1.134	170
5	1.037	46	18	1.142	181
6	1.045	56	19	1.152	193
7	1.052	65	20	1.162	206
8	1.060	75	22	1.180	229
9	1.067	84	24	1.200	255
10	1.075	94	26	1.220	281
11	1.083	104	28	1.241	309
12	1.091	115	30	1.263	339
13	1.100	126			

2. *Sulphuric Acid*.—Beaumé's areometer <sup>2</sup> will give a rough indication of the strength of this acid, using Lunge and Isler's table. Sulphuric acid is estimated by a normal solution of caustic soda, the strength of which has been tested in presence of phenol phthalein, for example, by a normal solution of pure oxalic acid containing 63 grammes per litre, or by normal sulphuric acid 49 grammes per litre. One hundred grammes of the sulphuric acid to be tested are weighed out, made up to a litre with water at the ordinary temperature, then 10 c.c. are drawn off, a few drops of an indicator like phenol phthalein added, and the normal soda solution run in. N being the number of cubic centimetres of soda added to cause the indicator to change colour, the percentage of sulphuric acid is calculated from the equation

$$N \times 0.049 \times 100.$$

<sup>1</sup> Or lb. of lime in 100 imperial gallons.

<sup>2</sup> Twaddell's hydrometer is invariably used in Britain.—Tr.

B. *Analysis of Finished Products : 1. Pyrolignite of Lime.*—

A fair average sample is taken representing the bulk of the batch of pyrolignite of lime, of which an exact analysis is to be made. Several processes are employed to determine the strength of pyrolignite of lime: (1) 10 grammes of pyrolignite of lime are triturated in a test glass on foot or a mortar with boiling water; the liquid is filtered, and the lime precipitated in the filtrate by ammonium oxalate. The precipitate of oxalate of lime formed is filtered off after a short time, then washed and dried; it is then moistened with nitric acid and calcined. The lime obtained is weighed after cooling. The amount of acetic acid necessary to saturate the lime found is determined by calculation, by multiplying the weight of the lime by  $\frac{120}{56} = 2.143$ .

By this process, it is taken for granted that all the lime which is dissolved in water is in the state of pyrolignite, which of course is not the case, the result obtained being a little too high, because, as already mentioned, pyrolignite contains free lime. (2) 100 grammes of pyrolignite of lime are treated with 90 grammes of commercial hydrochloric acid; the substances are left in contact for some hours, after which the liquid is distilled in a tubulated retort, fitted with a safety funnel and a condenser; when the distillation of the acetic acid appears to be finished, 100 grammes of water are added to the retort and the distillation and addition of water continued, so long as the liquid collected has an acid reaction. The liquors A, the product of the distillation, are mixed and brought to a given volume, of which 10 c.c., for example, are taken for titration with a solution of normal soda. As the hydrochloric acid added in excess distills with the acetic acid, a certain correction must be made, which is determined by the estimation of the hydrochloric acid contained in 10 c.c. of solution A. This titration is carried out by exactly neutralising 10 c.c. with a solution of pure carbonate of soda free from chlorine; a few drops of a saturated solution of neutral chromate of potash are added, then from a graduated burette a standard solution of nitrate of silver is run in until the liquid becomes faintly red; all the chloride of silver is then precipitated. In that way the amount of hydrochloric acid in solution A is determined, after correcting for this the weight of acetic acid contained in 100 grammes of the pyrolignite of lime is deduced. (3) 2 grammes of finely pulverised pyrolignite of lime are run into a 500 c.c. flask, then 20 c.c. of pure phosphoric acid of 45° B. (91° Tw., sp. gr. 1.455). The flask is fitted with an india-rubber cork with two holes, through one of these passes a delivery tube, which conveys the distilled vapours to a condenser; through the other passes a tube drawn out to a point which, reaching near to the bottom of the flask, conveys steam.



produced in another flask through the liquid. The acetic acid liberated by the phosphoric acid is entrained by the steam, and is carefully condensed, until the liquid which flows away is neutral to litmus. To attain this result, from eight to ten hours must be allowed for the operation and at least a litre of acid water must be collected; by titration and a simple calculation the amount of acetic acid, in the pyrolignite of lime tested, is determined. This method is frequently followed at the present time, owing to its exactitude, whilst at the same time it entails but little supervision. This method has been modified by Frésenius as follows: (4) 5 grammes of pyrolignite of lime and 50 c.c. of phosphoric acid 45° B. are run into a 200 c.c. long-necked flask also fitted with a cork with two holes. The mixture is cautiously heated without passing steam, then the heat is increased and afterwards reduced as soon as the mass assumes a very pasty appearance. The whole is allowed to cool slightly, and steam injected until the distillate has reached a volume of about 150 to 200 c.c.

*Lime.*—To estimate rapidly the amount of lime in a pyrolignite moisten the pyrolignite lightly with nitric acid, then calcine in a muffle furnace, cool and weigh. This gives the total lime.

2. *Acetates other than Acetate of Lime.*—The acetic acid is estimated by one of the methods previously given, preferably the third method.

TABLE XXVI.—SHOWING THE PERCENTAGE OF ACETATE OF SODA IN SOLUTIONS OF THE SALT OF VARIOUS DENSITIES

Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.
1.0058	1	1.0488	9	1.0910	17	1.1440	26
1.0116	2	1.0538	10	1.0966	18	1.1506	27
1.0174	3	1.0591	11	1.1074	20	1.1572	28
1.0232	4	1.0644	12	1.1134	21	1.1638	29
1.0292	5	1.0697	13	1.1194	22	1.1706	30
1.0341	6	1.0750	14	1.1254	23	—	—
1.0390	7	1.0802	15	1.1314	24	—	—
1.0439	8	1.0856	16	1.1374	25	—	—

In the case of a solution of acetate of soda, the above table will give the strength of the solution. Finally, if the amount of lead is to be determined in an acetate of lead, it is estimated as sulphate. It suffices to calcine a known weight of the lead salt in a porcelain crucible, previously moistening it with nitric acid, then by a few drops of sulphuric acid.

3. *Titration of Acetic Acid.*—The titration of acetic acid is effected either by volume or by weight. The French excise

method *by volume* is as follows: From 50 to 100 c.c. of the acetic acid to be titrated, diluted according to its strength with one, two or three times its volume of water, are run into a graduated 250 c.c. flask. The solution is afterwards intimately mixed, and a known volume of it is then run into another flask and two drops of a solution of phenol phthalein are added, then a normal solution of caustic soda is run into it gently until a permanent rose coloration appears, taking care to shake after each addition of soda. By a simple calculation the strength of the acetic acid is determined. 1 c.c. of normal soda solution = 0.060 gram of acetic acid.

To estimate the acetic acid *by weight*, 50 grammes of this acid are weighed exactly into a 500 c.c. flask, and the liquid made up to the mark with distilled water, then 10 c.c. are drawn off with a graduated pipette and run into a test glass, phenol phthalein is added, and a decinormal solution of soda run in from a Mohr's burette, with constant stirring, until a rose coloration appears. By multiplying the number of cubic centimetres of soda solution required for neutralisation by 0.6 the weight of acetic acid contained in 100 grammes is obtained. Mohr has given the following table of the densities of mixtures of acetic acid and water.

TABLE XXVII.—SHOWING THE PERCENTAGE OF GLACIAL ACETIC ACID IN MIXTURES OF ACETIC ACID AND WATER OF VARIOUS DENSITIES (MOHR)

Per cent.	Density.	Per cent.	Density.	Per cent.	Density.	Per cent.	Density.
100	1.0635	82	1.073	64	1.068	46	1.055
99	1.0655	81	1.0732	63	1.068	45	1.055
98	1.067	80	1.0735	62	1.067	44	1.054
97	1.068	79	1.0735	61	1.067	43	1.053
96	1.069	78	1.0732	60	1.067	42	1.052
95	1.070	77	1.0732	59	1.066	41	1.0515
94	1.0706	76	1.073	58	1.066	40	1.0513
93	1.0708	75	1.072	57	1.065	39	1.050
92	1.0716	74	1.072	56	1.064	38	1.049
91	1.0721	73	1.071	55	1.064	37	1.048
90	1.073	72	1.071	54	1.063	36	1.047
89	1.073	71	1.071	53	1.063	35	1.046
88	1.073	70	1.070	52	1.062	34	1.045
87	1.073	69	1.070	51	1.061	33	1.044
86	1.073	68	1.070	50	1.060	32	1.042
85	1.073	67	1.069	49	1.059	31	1.041
84	1.073	66	1.069	48	1.058	30	1.040
83	1.073	65	1.068	47	1.056	29	1.039

When a very dark-coloured acetic acid has to be titrated, such as pyroligneous acid, for example, it cannot be done directly. In that case 10 c.c. or 10 grammes of the acid to be tested are run into a small flask on to an excess of barium carbonate,

the exact weight of which is known. The whole is boiled; barium acetate forms which dissolves; the excess of barium carbonate is filtered off and well washed; the filter and its contents are then placed in a beaker, with a few drops of tincture of litmus, then a standard solution of nitric acid is added, until the liquid is acid and evolves no more carbonic acid on heating. The solution is then neutralised by a standard alkaline solution. The amount of carbonate of baryta left undissolved by the acetic acid is thus determined, the amount dissolved representing the weight of the acetic acid contained in the pyroligneous acid.

TABLE XXVIII.—SHOWING CONGEALING-POINT OF DILUTE ACETIC ACID OF DIFFERENT STRENGTHS.

Water added to 100 Parts of Acetic Acid.	Percentage of Water con- tained in the Acetic Acid.	Congee- ling- Point.	Water added to 100 Parts of Acetic Acid.	Percentage of Water con- tained in the Acetic Acid.	Congee- ling- Point.	Water added to 100 Parts of Acetic Acid.	Percentage of Water con- tained in the Acetic Acid.	Congee- ling- Point.
		°C.			°C.			°C.
0	0	+16.7	5	4.761	+9.4	12	10.714	+2.7
0.5	0.497	+15.65	6	5.660	+8.2	15	13.043	-0.2
1	0.980	+14.80	7	6.542	+7.1	18	15.525	-2.6
1.5	1.477	+14	8	7.407	+6.25	21	17.855	-5.1
2	1.961	+13.25	9	8.257	+5.3	24	19.855	-7.4
3	2.912	+11.95	10	9.090	+4.3			
4	3.846	+10.50	11	9.910	+3.6			

TABLE XXIX.—SHOWING THE DENSITIES OF MIXTURES OF ALCOHOL AND WATER CONTAINING, PER 100 VOLUMES,  $n$  VOLUMES OF ABSOLUTE ALCOHOL ( $n$  = DEGREES GAY-LUSSAC)

Alcohol per cent.	Density.	Alcohol per cent.	Density.	Alcohol per cent.	Density.	Alcohol per cent.	Density.	Alcohol per cent.	Density.	Alcohol per cent.	Density.
1	0.999	18	0.978	35	0.960	52	0.932	69	0.893	86	0.848
2	0.997	19	0.977	36	0.959	53	0.930	70	0.891	87	0.845
3	0.996	20	0.976	37	0.957	54	0.928	71	0.888	88	0.842
4	0.994	21	0.975	38	0.956	55	0.926	72	0.886	89	0.838
5	0.993	22	0.974	39	0.954	56	0.924	73	0.884	90	0.835
6	0.992	23	0.973	40	0.953	57	0.922	74	0.881	91	0.832
7	0.990	24	0.972	41	0.951	58	0.920	75	0.879	92	0.829
8	0.989	25	0.971	42	0.949	59	0.918	76	0.876	93	0.826
9	0.988	26	0.970	43	0.948	60	0.915	77	0.874	94	0.822
10	0.987	27	0.969	44	0.946	61	0.913	78	0.871	95	0.818
11	0.986	28	0.968	45	0.945	62	0.911	79	0.868	96	0.814
12	0.984	29	0.967	46	0.943	63	0.909	80	0.865	97	0.810
13	0.983	30	0.966	47	0.941	64	0.906	81	0.863	98	0.805
14	0.982	31	0.965	48	0.940	65	0.904	82	0.860	99	0.800
15	0.981	32	0.964	49	0.938	66	0.902	83	0.857	100	0.795
16	0.980	33	0.963	50	0.936	67	0.899	84	0.854		
17	0.979	34	0.962	51	0.934	68	0.896	85	0.851		

4. *Analysis of Crude Wood-Spirit. Alcoholometry.*—The use of alcoholometers, say Gay-Lussac's, Richter's or Tralles', gives directly the approximate percentage of pure alcohol contained in crude wood-spirit.

If the temperature be over 15° C. it is necessary to deduct 0·4 alcoholometric degrees for each 1° C. in order to find the alcoholic strength. If the temperature is below 15° C. it is necessary to add this figure.

Tralles' table differs slightly from that of Gay-Lussac. It gives the alcoholic strength at 15·56° C. Taking T as the strength in degree Tralles and D the density at 15·56, we get:—

TABLE XXX.—SHOWING THE DENSITY OF ALCOHOL OF VARIOUS STRENGTHS ACCORDING TO TRALLES.

T = 0	D = 0·9991	T = 50	D = 0·9335	T = 85	D = 0·8488
10	0·9857	60	0·9126	90	0·8332
20	0·9751	70	0·8892	95	0·8157
30	0·9646	75	0·8765	100	0·7939
40	0·9510	80	0·8631		

To get the percentage of alcohol *by weight* ( $x$ ) from the percentage by volume determined by the alcoholometer (V), the density of the mixture in the table (D) is taken and that of pure alcohol 0·795, and the following formula used,  $x = V \frac{0·795}{D}$ . In Germany alcoholometers giving the percentage by weight at 15° C. are employed.

*Determination of Methyl Alcohol.*—This method consists in converting methyl alcohol into methyl iodide which is weighed. In a small flask 22 grammes of iodine are dissolved in 5 grammes of methyl alcohol to which its own bulk of water has been added; the flask is corked, shaken, and left for ten to fifteen minutes in a bath of cold water to bring it to the ordinary temperature, then 2 grammes of phosphorus are added and the flask is attached to a vertical condenser. About a quarter of an hour afterwards, the temperature of the water is gradually increased to 75° C., shaking the mixture from time to time; the water bath is kept from a quarter of an hour to twenty minutes at that temperature, then it is allowed to cool. The methyl iodide formed is distilled, condensed, and collected in a graduated cylinder. Working on 5 c.c. of wood-spirit, the number of cubic centimetres of methyl iodide found, multiplied by 12·94, gives percentage by volume of real methyl alcohol.

*Determination of Acetone.*—Several methods may be employed for the estimation of acetone.

*Kramer's Method.*—This method is based on the conversion

of acetone into iodoform by iodine in presence of an alkali. The wood-spirit is diluted so that it contains 1 per cent. of acetone. A rough test is first made. One c.c. of the diluted wood-spirit is run into a flask with stopper with 10 c.c. of double normal soda (80 grammes of  $\text{NaHO}$  per litre). The whole is shaken and 5 c.c. of a double normal solution of iodine (254 grammes of iodine per litre) added. Iodoform is formed, which is dissolved by shaking with 10 c.c. of ether free from alcohol, the volume of the ethereal layer is read off and 5 c.c. of it taken and evaporated on a watch glass, placed in a desiccator over sulphuric acid. From the weight of iodoform found the percentage of acetone is calculated: 1 molecule of iodoform 394 = 1 molecule of acetone, or 58.

*Messinger's Volumetric Method.*—This method is based on the reaction described above, but with excess of iodine in alkaline solution, which is afterwards estimated by sodium thiosulphate, the solution having been previously acidified. The solutions used are: (1) A solution of sublimed iodine  $\frac{1}{2}$  normal, or 25.4 grammes per litre, which is dissolved by double its weight of potassium iodide. (2) Solution of  $\frac{1}{2}$  normal sodium thiosulphate, or 12.41 grammes pure air dried per litre, dissolved in distilled water, to which 15 c.c. of caustic soda solution has been added. These two solutions should be strictly exact, that is to say 1 c.c. of the standard iodine solution should correspond to 4 c.c. of the standard hyposulphite solution. (3) Solution of *caustic soda* obtained by dissolving 1 kilogramme of caustic soda in flakes and the solution made up to 10 litres. (4) Sulphuric acid solution made from 275 c.c. of sulphuric acid 66° B. (168° Tw.), sp. gr. 1.840, in enough distilled water to make 5 litres. (5) Starch paste made by stirring up 5 grammes of starch in 500 c.c. of distilled water, boiling for an hour, then completing to 1 litre with salt water. To obtain good results, the product to be analysed should contain about 0.5 per cent. of acetone. By means of a pipette graduated in two places, 20 c.c. of the liquid to be analysed is run into a 1 litre flask already containing a certain amount of distilled water free from nitrites or organic matter. The volume is made up to 1 litre, and the flask and contents well shaken to render the liquid perfectly homogeneous. Into a 250 c.c. flask with a ground glass stopper, containing already 30 c.c. of double normal soda, there are run 20 c.c. of the dilute solution, the acetone content of which it is desired to ascertain. After mixing, 55 c.c. of the  $\frac{1}{2}$  iodine solution are added from a burette. The whole is again agitated and allowed to react fifteen to twenty minutes. Then 35 c.c. of normal sulphuric acid are added, and the liberated iodine is titrated with the thiosulphate, which is run in from a graduated burette until the solution is almost decolorised. At this moment 4 to 5 c.c.

of starch paste are added, and thiosulphate is dropped in gradually until complete decolorisation is effected. Let  $N$  be the number of cubic centimetres of thiosulphate solution used,  $\frac{N}{4}$

will correspond with the iodine in excess, from which the iodine combined with the acetone can be deduced. This amount of iodine multiplied by 0.0762 gives the percentage of acetone contained in the liquid to be estimated. Two parallel experiments are generally made, one with a typical methyl alcohol, obtained by adding 25 per cent. of pure acetone to pure methyl alcohol, the other with the sample to be tested. When the operator has had no experience in this method of analysis, it would be well to perform the determinations in duplicate. This process is used in the laboratory of the French Minister of Finance.

*Denigès' Method (Journal de Pharmacie et de Chimie, 1899, ix., 7)* is based on the property of acetone to yield a crystalline precipitate with excess of mercuric sulphate, the formula of which is  $[(\text{HgSO}_4)_2 \cdot 3\text{HgO}]_2 \cdot 4\text{CO}(\text{CH}_3)_2$ , which dried at  $110^\circ \text{C}$ . ( $230^\circ \text{F}$ .) becomes  $[(\text{HgSO}_4)_2 \cdot 3\text{HgO}] \cdot \text{CO}(\text{CH}_3)_2$ .

*Estimation of Allyl Alcohol.*—This process is based on the property which allyl alcohol possesses of yielding an addition compound with bromine: one molecule of allyl alcohol absorbs two atoms of bromine. The solution of bromine used contains 7.2 grammes of bromine per litre; and it is prepared by dissolving in distilled water 2.508 grammes of potassium bromate and 8.936 grammes of potassium bromide, both dried at  $100^\circ \text{C}$ . ( $212^\circ \text{F}$ .), and the volume made up to 1 litre; 100 c.c. are taken for analysis, 20 c.c. of sulphuric acid of 1.29 density added, to which mixture the wood-spirit is added until the yellow coloration is discharged.

*Determination of the Impurities in Wood-Spirit.*—The method used is that of Rose, which consists in noting the increase in volume which a known volume of chloroform undergoes when agitated with methyl alcohol in presence of a solution of sodium bisulphite. The apparatus used is a bulb tube (Fig. 73), the lower portion of which, of 55 c.c. capacity, is graduated into tenths from 50 to 55 c.c.; 50 c.c. of pure chloroform at  $15^\circ \text{C}$ . are run into this tube from a burette with two marks, then a mixture of 25 c.c. of the methyl alcohol to be tested and 60 c.c. of distilled water. The whole is energetically shaken and allowed to stand in a bath of cold water at  $15^\circ \text{C}$ ., then the increase in volume of the chloroform solution is noted.

*Estimation of Ethers in Methyl Alcohol.*—This estimation is effected by a soda saponification, using 20 c.c. of the methyl alcohol which is run into a 200 c.c. flask with 50 c.c. of semi-normal caustic soda. The flask is connected with a reflux condenser and is boiled for half an hour, then the soda in excess is

titrated back with semi-normal sulphuric acid using phenol phthalein as indicator. The saponifiable products are calculated to methyl acetate by the formula

$$(50 - N) \times 0.037 \times 5,$$

N being the number of cubic centimetres of half normal sulphuric acid used.

5. *Assay of Pure Methyl Alcohol.*—(1) The methyl alcohol should register 99 per cent. by the alcoholometer, *i.e.* 0.7995 density at 15° C. (2) It must not contain more than 0.7 per cent. of acetone by Kramer's method. (3) On distillation, 95 per cent. ought to pass between two consecutive degrees C. of the thermometer. (4) With double its weight of sulphuric acid

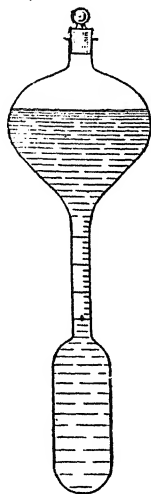


FIG. 73.—Rose's tube. FIG. 74.—Reduction tube.

of 66° B. (168° Tw., sp. gr. 1.84) it should give at the most a pale yellow. (5) It should remain colourless with an excess of caustic soda. (6) 5 c.c. should not immediately decolorise 1 c.c. of potassium permanganate solution containing 1 gramme per litre.

6. *Assay of Acetone.*—(1) It should be limpid and pale. (2) It should mix without turbidity or eventual precipitation with water in all proportions. (3) The acetone should be neutral and mark 98.5 per cent. at 15° C. (59° F.) by the alcoholometer. (4) On distillation 95 per cent. of the liquid should distil at 58° C. (136.4° F.). (5) A solution of mercuric chloride should give no turbidity with acetone. (6) The acetone should not contain more than 0.1 per cent. of aldehyde, which is determined by reduction with a solution prepared from 30 grammes of nitrate of

r, 30 grammes of caustic soda, and 200 grammes of ammonia (0.900 density), all dissolved in distilled water to 1 litre; 5 c.c. of acetone are taken, its volume of distilled water and 1 c.c. of the silver solution added; it is then left for a quarter of an hour in darkness, and subsequently tested with ammonium hydrosulphide to see if there be nitrate of silver in excess; if not the solution contains more than 1 per cent. of aldehyde. (7) By Singer's iodometric assay 98 per cent. at least should be obtained.

7. *Assay of Creosote*.—Beech-wood creosote being highly impure, impure products and even ordinary carbolic acid are sometimes substituted for it in commerce; sometimes it is mixed with alcohol, or oily matters, fixed and volatile. All creosotes when run into water drop by drop, do not fall to the bottom, which become turbid after slight agitation should be rejected. To distinguish carbolic acid from creosote or to detect its admixture with the latter, one of the following methods may be employed: (1) By mixing equal volumes of creosote and glycerine the former is not dissolved, whilst carbolic acid dissolves completely therein and is not precipitated by the addition of water; ammonia does not dissolve creosote, whilst (when hot) it slightly dissolves carbolic acid; (3) a slightly ammoniacal solution of perchloride of iron colours creosote green in this reaction 1 part of creosote in 500 parts of carbolic acid (easily be detected); an aqueous solution of perchloride of iron added to creosote is not changed in colour, whereas it becomes violet with carbolic acid. To detect small amounts of carbolic acid in creosote, a few drops of the latter are boiled with 6 to 8 c.c. of nitric acid until no more red fumes are given then a solution of potash is added when cool. If an immediate yellow precipitate or coloration of picrate of potash is produced, this indicates the presence of carbolic acid in the creosote. To detect alcohol mixed with the creosote, the creosote is distilled and the first runnings are collected, or better, ten times its weight of sweet almond oil is added to the product; there be only 0.4 per cent. of alcohol the mixture becomes aqueous and remains so after agitation.

*Fixed or volatile oils* are easily detected. By pouring a little of the liquid on paper a spot will be formed, which remains transparent when cold if essential oil be present and does not change appearance under the action of heat in the presence of fixed oils. By adding to a known weight of the suspected creosote a sufficient quantity of acetic acid, the fatty substances soluble in the acid may be isolated whilst the creosote dissolves.

8. *Analysis of Carbonate of Potash*: (1) *Moisture*.—Dry 10 grammes of the product over a bunsen burner until no water is driven off and determine the loss in weight.



(2) *Insoluble Matter*.—Dissolve 10 grammes of carbonate of potash in hot water, filter through a tared filter, make up to 500 c.c. with the wash water; dry the filter and contents, ignite and weigh the insoluble residue.

(3) *Alkalinity*.—Draw off 50 c.c. of solution from 2 and determine the total alkalinity as potassium carbonate by standard acid, using methyl orange as indicator.

*Estimation of Soda in Potash*.—By Graeger's process, which consists in dissolving 6.911 grammes in 100 c.c. of water, collecting and weighing the insoluble residue, then in determining, volumetrically, in a portion of the solution the combined hydrochloric and sulphuric acids which are converted by calculation into potassium salts and the weight of the pure alkaline carbonates determined by difference. The carbonates are then titrated by a normal solution of nitric acid (63 grammes  $\text{HNO}_3$  per litre) corresponding to 69 grammes  $\text{K}_2\text{CO}_3$ . The ratio of the carbonates is given by the following table:—

TABLE XXXI.—SHOWING THE NUMBER OF CUBIC CENTIMETRES OF NORMAL ACID REQUIRED TO NEUTRALISE 1 GRAMME OF A MIXTURE OF THE CARBONATES OF POTASH AND SODA IN VARIOUS PROPORTIONS

Grammes $\text{K}_2\text{CO}_3$ .	Plus grammes $\text{Na}_2\text{CO}_3$ .	Require Normal Acid in c.c.	Grammes $\text{K}_2\text{CO}_3$ .	Plus grammes $\text{Na}_2\text{CO}_3$ .	Require Normal Acid in c.c.
1.00	0.00	14.47	0.45	0.55	16.89
0.95	0.05	14.69	0.40	0.60	17.11
0.90	0.10	14.92	0.35	0.65	17.33
0.85	0.15	15.14	0.30	0.70	17.55
0.80	0.20	15.35	0.25	0.75	17.76
0.75	0.25	15.57	0.20	0.80	17.97
0.70	0.30	15.79	0.15	0.85	18.19
0.65	0.35	16.01	0.10	0.90	18.40
0.60	0.40	16.23	0.05	0.95	18.62
0.55	0.45	16.45	0.00	1.00	18.84
0.50	0.50	16.67			

The amount of soda contained in a potash salt may be determined by difference, the potash being estimated by one of the undernoted processes.

*Estimation of Potash*.—Three different processes may be adopted: (1) The platonic-chloride process; (2) Schloesing's perchloric acid process; (3) Carnot's volumetric process.

*Platonic-chloride Process*.—Five grammes of carbonate of potash are dissolved in water containing hydrochloric acid, an excess of baryta water added, and the precipitate of sulphate, silicate, and phosphate of baryta filtered off. A current of carbonic acid gas is passed through the solution, and the operation is terminated by boiling, so as to decompose the resulting soluble

bicarbonate of baryta. The liquid is then filtered from the insoluble carbonate of baryta, into which the excess of baryta water has been converted. The liquid, to which hydrochloric acid has been added, is evaporated in a 40 to 50 c.c. capsule, then platinic chloride is added drop by drop, and the whole evaporated on the water-bath till the mass becomes pasty; it is then withdrawn from the fire, and a mixture of alcohol and ether, consisting of 9 parts of 85 per cent. alcohol and 1 part of 65 per cent. ether is added; the whole is triturated for some time to wash the potassium platino chloride which is formed, and which is insoluble in this liquid, and the precipitate is collected on a dry tared filter. This method requires much care; the following, which is more rapid, is preferred. It consists in the immediate formation of the potassium platinochloride. One gramme of the carbonate of potash is dissolved in a little water, and hydrochloric acid added. The solution is concentrated, then platinum chloride solution (10 grammes per 100 c.c.) added, until no further precipitation takes place; the whole is then evaporated; if the residue becomes white on the sides this indicates that an insufficient quantity of platinum chloride solution is present, and more must, in that case, be added. Then the alcohol and ether mixture is added, the whole filtered through asbestos (Fig. 74), and the precipitate washed with ether-alcohol, until there is no more platinum in the filtrate (rose colour with potassium iodide). The tube is dried in the water-bath, then a current of hydrogen is passed through the tube which is heated, so as to transform the salts into metallic platinum, the potassium chloride is washed out with hot water and the platinum is weighed:  $\text{Pt} \times 0.4825 = \text{K}_2\text{O}$ .

In this operation it is necessary to heat the tube gently, and to wait until it is full of hydrogen before bringing a flame near it. The total alkali is found by titration with standard sulphuric acid, from this is deducted the amount of potash found, the remainder is then calculated to sodium carbonate.

*Estimation of Potash by Schloesing's Process.*—Five grammes of the salt are dissolved in 40 c.c. of water and nitric acid, and evaporated to dryness. The residue is taken up by 20 c.c. of nitric acid, 20 c.c. of water and filtered; ammonia is added in excess to the clear solution to precipitate iron and alumina, and the precipitate filtered off and washed. The filtrate and wash waters are collected in a 100 c.c. flask which is made up to the mark with water. Then 20 c.c. are drawn off, to which an excess of barium nitrate is added to precipitate phosphoric and sulphuric acids. The filtered liquid is evaporated to dryness, then taken up by 5 c.c. of nitric acid and again evaporated. This operation is repeated twice. After the last operation 15 c.c. of a 10 per cent. solution of perchloric acid is added, and heat

applied to expel the excess of acid. Perchloric acid is prepared by treating ammonium perchlorate in the hot state with aqua regia. The reaction is effected in a glass flask. A mixture of perchloric and nitric acid is obtained containing a little hydrochloric acid which is slowly evaporated on a sand bath to expel all HCl and a part of the  $\text{HNO}_3$ . The heat is withdrawn when white fumes of perchloric acid begin to come off. After having expelled the excess of perchloric acid added to the potash salt, the mass is moistened with water, then the whole is washed with 85 per cent. alcohol, to dissolve the perchlorates—other than potassium perchlorate—which are simultaneously formed. The potassium perchlorate is collected on a small filter, washed with 85 per cent. alcohol, then dissolved by hot water; the solution is evaporated to dryness, and the weight of perchlorate found, multiplied by 0.3401 gives the percentage of  $\text{K}_2\text{O}$ .

*Volumetric Estimation of Potash by Carnot's Process.*—This method is based on the reaction which takes place when a potassium salt comes in contact with a bismuth salt and a thio-sulphate. A perfect, well-defined double thiosulphate of potassium and bismuth is formed, soluble in water, but precipitated in the form of a yellow powder on the addition of alcohol. In carrying out the process, if, for example, a sample of potassium chloride (muriate of potash) has to be tested, 5 grammes of the substance are taken, dissolved in 3 or 4 c.c. of water and 10 c.c. of a solution of bismuth chloride, 10 c.c. of thiosulphate of lime and 160 c.c. of alcohol added. The yellow precipitate is formed. After ten minutes the precipitate is filtered, washed with alcohol, and then redissolved in hot water, and the thiosulphate which it contains estimated. With this end in view, 5 c.c. sulphuric acid are added to the solution and a few drops of starch paste. A solution of standard iodine is then added until the characteristic blue iodide of starch is produced. The operation is conducted very rapidly, the double thiosulphate of potassium and bismuth being very easily decomposed. The solution of bismuth chloride is prepared by treating 100 grammes of basic nitrate of bismuth with hydrochloric acid and heating gently. The whole is allowed to cool, strong alcohol added, and after standing, filtered and the solution is then made up to a litre. The solution of thiosulphate of lime contains 200 grammes per litre. The iodine solution consists of 56.96 grammes of pure iodine and about 75 grammes of iodide of potassium per litre: 1 c.c. of this liquor corresponds exactly with 0.01 gramme of  $\text{K}_2\text{O}$ .

## CHAPTER VI

### THE DESIRUCTIVE DISTILLATION OF OLIVE OIL RESIDUALS

Wood waste from saw-mills, from factories for the extraction of dyes or of tannic acid from wood, and olive oil residuals are often used as fuel in the factories in which they are produced, whether to heat a stove or to raise steam. Ingenious furnaces with capacious grates and with steps or tiers and even gas generators have been patented with this end in view, but they involve great initial expense and frequent and costly enough repairs. Nevertheless, and in spite of this main use, as fuel and other secondary utilisations, to be referred to hereafter, the consumption of sawdust and olive residuum is feeble compared with their production ; that is why it has been rightly attempted to distil these products. As to the importance of distilling olive oil residuum (*grignons d'olives*) the following is the report of a lecture by D. Vladimir Guerrero of Smirnoff. Manufacturers know by experience that hard woods give the best yield in alcohol, acid, and charcoal, and that the latter is more dense than that obtained from soft wood. The charcoal obtained from olive residuum is still more dense than that from hard wood ; the former weighs 37 kilogrammes per hectolitre (81.4 lb. per 2 $\frac{3}{4}$  bushels). That of the oak, which is one of the hardest varieties of wood, 22 kilogrammes (say 48.4 lb. per 2 $\frac{3}{4}$  bushels). That is due not only to its granular form but also to its richness in carbon, an exceptional richness giving a greater number of calories on burning, an observation already made by users of charcoal from olive oil residuum. The thermal value of one charcoal compared with another is verified by the fact that the combustion of the most rich in carbon is, as we find to be the case with charcoal from olive oil residuum, accomplished completely and regularly without production of carbonic oxide. It has been known from time immemorial that a very pure black, for fine carbon colours, was manufactured in Spain from peach stones under the name of Spanish black. The ligneous tissues of the olive are essentially vascular. It consists, in fact, of: the seed, fatty, cellular, and vascular ; of the almost vascular kernel of the pulp, where the oil is found between the vascular and cellular tissue, and finally, of a hard, coriaceous skin, where a

substance termed *cutose*, which contains carbon and vasculose in equal proportion, predominates. The vascular richness of plants depends chiefly on a dry climate and the direct action of the solar rays. Vasculose richer in *carbon* but poorer in the elements of water is a dehydrated ligneous body when compared with cellulose, which is consequently a hydrated ligneous body, and it may be added that cellulose is the product of a moist climate and vasculose of a dry climate. The varieties of olives cultivated for oil are more ligneous, and thus give a larger amount of residuum than those cultivated for preserves. The proportion of residuum, which is at least 18 per cent., and which may rise to 30 per cent., is one-fourth of the bulk of the fruit. There are even varieties of olives in the province of Tarragona, for example, where the residuum weighs more than the pulp. Guerrero's experiments, verifying the previous investigations of eminent chemists, on the kernels of certain fruits, have demonstrated that olive oil residuals contain the vasculose from which methylic alcohol and acetic acid have been extracted for about 100 years, and that it is a useful source of raw materials for the pyroligneous industry. The wood wastes produced in several industries have been the subject of experiments, and more or less suitable plant for the extraction of pyroligneous products therefrom has been invented. Sawdust, which is very plentiful, has for a long time been utilised in wood distilleries, and it yields more or less interesting products according to whether it comes from a hard wood or a soft wood.

*Bergmann's Patent.*—Of late years attempts have been made to utilise the residuals from the extraction of tannin materials and dye woods. Bergmann's invention for this purpose was introduced in Germany in 1892. When applied it gave no results, or rather it gave disastrous results. Some people blamed the plant as badly planned by its inventor. But that was not the cause. Bergmann's plant gave bad results for the simple reason that the raw materials could not yield what they did not possess, *i.e.* they did not contain vasculose in the necessary proportion. Besides this there was another drawback: the raw materials contain much water, sometimes even as much as 60 per cent. and although bulky and of great weight contained very little utilisable material.

*Jurgensen's Patent.*—Subsequently, Dr. Rolof Jurgensen, following without doubt in Bergmann's tracks, brought out a process to treat all kinds of wood waste, including seeds and oleaginous fruits. Jurgensen, more fortunate than his predecessor, had the tact to distil olive oil residuum and obtained good results. He showed the products (alcohol, acid, etc.) extracted therefrom at the 1900 Paris Exhibition. Jurgensen, who experimented on large quantities, asserted that he had

obtained very variable, but always satisfactory results. His process consists in treating olive oil residuum in a form of extraction apparatus, but after previous drying, and for that he proposed to *press* them, being undoubtedly unacquainted with the method of treating olives. The carbonisation was effected in a plant (1900 pattern) intended to distil, in a continuous manner, not only olive oil residuum but also sawdust, tannic acid residues and the waste left after the extraction of dyes from wood or oil from oil seeds.

*Guerrero's Modification of Jurgensen's Process as applied to Olive Oil Residuum.*—When Guerrero examined Jurgensen's process with the view of verifying the practical results which had been obtained in the distillation of olive oil residuum, he made certain objections to Jurgensen's process, which he believed could be advantageously modified. Accordingly, aided by theoretical knowledge which is indispensable, he sought to find out the process which should be followed, before deciding upon the mechanical method, by which the process would be carried out. It was necessary to study the chemical and physical properties of the substance, and the first thing which he had to do was to investigate the composition of the different varieties of wood and of olive oil residuum. It was necessary to compare their density, bulk, shape, porosity, and other physical and hygrometric properties, and likewise to know their chemical composition starting from elementary analysis. It was also necessary to have a full knowledge of the industry, which is termed wood distillation. Guerrero therefore commenced, whilst visiting the different European factories, a series of experiments upon olive oil residuum—which he had caused to be sent to him from Spain—and upon several varieties of wood from different sources which he procured in the different factories which he visited; and then, placing himself in communication with the directors of the most famous laboratories of Paris, a plan was prepared for these investigations. Guerrero's researches are systematically expounded in that part of the memoir on the creation of the pyroligneous industry in Spain, which deals with experiments and analyses. Among other experiments made, attention may be drawn to the comparative hygrometric properties (to which allusion has been made, as one of the causes of the poor success of Bergmann) of wood and olive oil residuum, which are as follows: Olive oil residuum without oil normally contains 12 per cent. of moisture, on account of its crushed condition, but it soon dries, as the water it contains is insignificant, olive oil residuum not being a hygrometric substance. On the other hand, wood, which is felled a year before distillation, still contains, when placed in the retorts, a fourth of its weight of water (at the time of felling

it contains 45 per cent.). This difference means an economy in distilling residuum as compared with wood. Comparative tests showed that olive oil residuum contains both hard wood and soft wood, *i.e.* cellulose and vasculose (the pulp, the hard skin, and the *grignon*). This parallel established, and the properties of both substances being known, and also the advantage of carbonising vasculose rather than cellulose, an advantage which Guerrero early demonstrated, the facility of realising the distillation of olive oil residuum is a deduction therefrom. This inestimable advantage, impossible with wood, enables each substance to be treated appropriately. Guerrero, therefore, gave to the hard wood of olive oil residuum the name of *grignon riche* because it is rich in vasculose, and to the soft wood of olive pulp that of *grignon pauvre*. Such are the essential principles of Guerrero's process for extracting pyroligneous products from olive oil residuum. As to the mechanical system it could not be more simple; it is that of the coffee roaster. Olive oil residuum does not dry in the stove, as Jurgensen asserted. It is in vain to try it. It is dried in a sieve, by a fan, at the time it is separated into *grignons riches* and *grignons pauvres*. The *grignons riches* in the proportion of  $\frac{4}{5}$  is the substance to be distilled. The residual *grignon pauvre* is an organic manure which, if need be, may be used as fuel mixed with tar.

*Laboratory Experiments of Grandean and Aubin.*—The following are the results of numerous analyses and distillation experiments on olive oil residuum compared with wood:—

TABLE XXXII.—SHOWING THE AVERAGE PROXIMATE ORGANIC ANALYSES OF OLIVE OIL RESIDUUM AND WOOD

	Vascu- lose.	Cellu- lose.	Total.	Vascu- lose per cent.	Comparative Vascular Richness.	Comparative Ligneous Richness.
Wood (beech and oak) .	32.81	11.34	44.15	74.0	89	93
Olive oil residuum :—						
Rich kernel, 80 per cent.	36.83	10.45	47.28	80.0	100	100
Poor kernel, 20 per cent.	19.34	5.74	25.08	76.0	52	44

If we compare the factory results in column D with those obtained from wood in the European carbonisation factories, the superiority of olive oil residuum is manifest. The pyroligneous yield of wood is less by one-fifth part than that obtained from the distillation of olive oil mill residuals. Such then are the results obtained as regard extracted products. The methyl alcohol and acetic acid obtained were the first obtained in the pure state from olive oil residuum.

TABLE XXXIII.—SHOWING THE AVERAGE RESULTS PER CENT. OF DISTILLING ASSORTED AND UNASSORTED OLIVE OIL RESIDUALS AS COMPARED WITH WOOD

	A.	B.	C.	D.	E.	F.
Methyl Alcohol . .	1.17	1.60 <sup>1</sup>	1.20	1.38	100.0	86.0
Acetic Acid <sup>2</sup> . .	4.51	3.18	3.25	4.07	100.0	79.0
Tar . . . .	7.12	10.00	5.75	8.0	100.0	71.0
Charcoal . . . .	29.00	37.00	25.50	31.7	100.0	80.0

A = *Grignons Riches* (Grandean and Aubin). B = *Grignons Ordinaires*, without separating the *Grignons Riches*. Average factory results obtained in the Ivry-sur-seine wood distillery. C, Wood, average between pine, spruce, and oak. D, olive oil residuum, average between the *grignon ordinaire* and the *grignon riche*. E and F, comparative results, olive oil residuum yielding 100 lb. of each product, then the same weight of wood yields the amount given under F.

*Actual Working of Olive Oil Residuals. Extraction of the Oil from the Residuals. The Charcoal from the Residuals and its Applications.*—The production of oil in Spain varies greatly from one year to another, so much so that in certain districts it is almost *nil*, whilst in other and even neighbouring districts it is very abundant. For example, one year will give a produce of one, the following year of three, another year of five, or *vice versa*, but the averages of each five years are almost the same. These differences of production are due, in the first place, to the natural condition of the plantations being in dry soil, with no means in nine-tenths of the plantations for applying irrigation; they are, therefore, exposed to meteorological changes, which do not harmonise very well with the rainfall, where these plantations abound. (A fresh proof of the want of forests.) These differences are also due to the poor regard we have for trees, which, like everything else, are grateful when well tended. Every one knows that this want of regard is due to a want of money, that is to say, of the working capital necessary for good farming, but very often this capital is there, and then it is the cultivation that is at fault, when it is not caused by excessive neglect. In a memoir presented to the Paris Exhibition of 1900, Manuel Porcer y Ruidor, who belongs to a family of olive-tree cultivators, where they appreciate the olive-tree, and where Guerrero knew by experience that the olive-trees bear fruit, estimates that the production of oil in Spain amounts to 2,900,000 hectolitres (63,800,000 gallons) in agreement with Dr. Monjarres of Seville. Guerrero believed that the production might, without exaggeration, be estimated at 2,700,000 hectolitres (59,400,000 gallons); by allowing for an extreme production of a fifth part, more or less, the figures would be 2,100,000

<sup>1</sup> 7.38 of 20 per cent. phlegms.<sup>2</sup> Glacial.



and 3,200,000 hectolitres (46,200,000 gallons and 70,400,000 gallons), which is equal to an annual average of 230 kilogrammes (506 lb.) per hectare (*i.e.*, per 2.47 acres), or say 205 lb. per acre. Consequently, the ratio of residuum to oil being known, there would be 409 kilogrammes of these residues per hectare, or say 364 lb. per acre per annum.

The figures given by Guerrero are those of 1898, a year when the production was inferior to the average; of thirty-three productive provinces, eleven only had a good yield. The total production was 1,900,000 hectolitres (41,800,000 gallons), of which 1,270,000 hectolitres (27,940,000 gallons) were produced in the districts of Andalusia and Estremadura. Three provinces, that of Jaen, Cordova, and Seville, produced nearly 1,000,000 hectolitres (22,000,000 gallons), that of Jaen alone 500,000 hectolitres (11,000,000 gallons), say the fourth of the whole production. That district has the largest production in Spain, and it is to it that the others go to purchase the residuals for extraction. What is done with this enormous mass of woody fibre? Without counting exportation, which is insignificant, Guerrero estimated that 200,000 tons are utilised in the hundred odd oil mills, and that the rest is used as fuel; it is in fact the fuel used in the oil-producing countries, where the *grignon* replaces the scarce and dear wood. The oil residuals are employed for domestic purposes (kitchens and brasiers) in the manufacture of *grignon* charcoal, of lime, bricks, and other industries. It is also used in the feeding of pigs and poultry; but frequently these residues are thrown into the stables. They lose in open air by slow combustion a third of their weight, without profit to any one. The 350,000 tons of oil residuals are produced on 1,150,000 hectares (2,840,500 acres), the area under olive cultivation in Spain according to statistics. To find the forest surface necessary to produce this quantity of ligneous matter in the form of wood, such as oak, it suffices to know that this tree, arranged for felling at intervals of twenty years, produces in a good soil 35 tons per hectare (14 tons per acre) at the end of twenty years. Consequently, 350,000 tons of wood would require 10,000 hectares (24,700 acres), and for twenty years, one felling every year, twenty equal surfaces, say 200,000 hectares (500,000 acres). The value of olive oil residuum for the manufacture of pyroligneous products having been demonstrated, it follows that there are in Spain 200,000 hectares (500,000 acres) of virgin forest, much more productive than if it were planted with oak, which only wants a little initiative to exploit. The industry of extracting the oil from the residuals, with which, beyond the previous applications, no one knew what to do, has increased their value. With the installation of these factories they have risen (in Andalusia) from five

pesetas, the price still current in some districts of the province of Jaen and other regions, to twenty and even thirty pesetas the ton, which is the average for five years. For several years the dry residuals were only used as fuel in the same factories, but large quantities remained piled up in the yards, up to the day when the idea came to convert them into charcoal known under the name of kernel or *grignon* charcoal. This manufacture became more general in proportion as the excellence of the new fuel became better known. This charcoal is now made in many Andalusian villages, and its production increases every year, as users prefer it to vegetable charcoal for many purposes. A few years ago *grignon* was sold with difficulty at 1.25 pesetas the hectolitre ( $2\frac{3}{4}$  bushels); to-day whole waggons are charged with it for the North, or Madrid, for example, where it is sold at 5.50 pesetas the hectolitre.

In spite of that, coal, especially Andalusian, the calorific intensity of which varies between 4500 calories and 6500 calories, according to the proportion of ash, has been replaced by olive oil residuals in many industries, and the manufacturers who use this combustible would not change it for coal of average quality. The *grignon* in fact produces 4500 to 5000 calories when it is dry, but has the inestimable advantage of not making any clinkers. The experiments of Dr. Monjarres yielded still better results than those quoted. It follows from the latter experiments that olive oil residuals have a greater number of calories, by half, than wood, and this demands attention, because it confirms what Guerrero demonstrated by comparative analysis between these residuals and wood. Monjarres' experiments gave 5270 calories for residuals and 3600 for wood. The experiments quoted above, and the results attained in the actual practice of this industry, confirm Guerrero's practical scientific demonstrations, that is to say, the vascular riches of a residual neglected up to the present time, but which as a raw material for the production of methyl alcohol and acetic acid is without equal. It will be readily understood that the carbonisation of olive oil residuals, in closed vessels, would advantageously replace the distillation of wood, supposing that the wood distilling industry had been already successfully established in Spain, but there is no wood for rational working; on the contrary, however, vasculose, the raw material for that industry, exists in abundance in olive oil residuals. Of the actual production of residuals, rather more than half is used to make *grignon* oil (*l'huile de grignon*); a very important amount still remains. If this utilisation is carried further, by combining oil extraction and carbonisation, a great saving would be made, because the cost price of the methyl alcohol and acetic acid, as well as their compounds and derivatives, would be very

appreciably reduced. An idea of cost may be obtained by taking into account the fact that the residuals give a greater yield in acetic acid and wood-spirit, that labour is cheaper than here, and that the raw material, the de-greased olive oil residual, costs less, especially when oil extraction and carbonisation, the most rational way of working, are carried out in the same factory. What competition is to be feared since wood costs at least twenty francs (sixteen shillings) the ton? If the enormous quantity of rich ligneous material contained in olive oil residuum could be distilled very quickly, that would occasion a marked change in the pyroligneous product market. That outlook is, however, not to be feared, because the consumption of these products increases daily owing to the developments of industry, and because this exploitation of olive oil residuals cannot become completely developed for a relatively long time. In any case, the advantage would be, for Spain, that there would be no need to import either acetic acid or acetates, and if need be Spain could export its products which need not fear any competition so long as acetic acid and methylic alcohol continue to be made from twenty-year-old oaks and beeches. The riches which would be created with the new profit of these residues is of capital importance for Spain.

At the present prices (the cost diminished by  $\frac{1}{3}$ ) the extraction of oil would represent 26,000,000 pesetas, carbonisation 34,000,000, and between the two one-third the value of the oil, supposed to be only 180,000,000, calculating on an average of 2,700,000 hectolitres, or 243,000 tons of olive oil, at 750 pesetas the ton. Looking to the importance of wood distillation and the favourable conditions for establishing this industry in Spain with olive oil residuals, it may be asked, "Why has it not been done before?" To which it may be replied, "Because the time had not come for it to be done". But another explanation must be forthcoming. The industry proper flourishes only in well-wooded countries because the raw materials are abundant there. It is, moreover, natural that residues which are only produced in large enough quantities in Spain should be passed by unseen. That is explained by the insignificant consumption of pyroligneous products in Spain, compared with other countries, and also because of the methodical nature of the Spaniard, who has little inclination for new industries; these riches, like many others, have remained untouched. Owing to the intensive felling of forests to supply the pyroligneous industry and its derivatives, as well as for paper manufacture, the price of wood, which continues to rise, leads to an increase in the price of the products in proportion as their uses increase. At the 1900 International Congress of Applied Chemistry, held at Paris, Dr. Jurgensen urged that investigations be undertaken so as to place other raw

materials at the service of wood distillers, especially cheap waste products, which could be used to produce acetic acid more cheaply. Dr. Jurgensen might have added that such utilisation of waste products could be made to harmonise with the planting of forests (somewhat advanced in his country), because the industry, which consists in felling twenty-year old trees, appears a little drastic. This desire is exactly realised in Spain, where the olive produces a residue rich in vasculose, a material which, as Guerrero has demonstrated, is the best that could be chosen, and which at even the same price might advantageously compete with wood. A triumph might thus be realised by Spain in the battles which industrial nations wage against one another. A good opportunity presents itself for following up the industrial reawakening of Spain, quite remarkable these last four years, as regards agricultural, chemical, metallurgical, and other industries which have been installed without the aid of foreign capital. It is to be hoped that the new industry, essentially a chemical one, will very soon be inaugurated, and assist much to create those large chemical factories in Spain which gave so much supremacy to Germany. Numerous chemical industries can be made to live in Spain. Amongst others, the manufacture of colours, margarine, glycerine, the manufacture of soda, and thus utilise numerous residues now almost all waste products. Everything in Spain favours the creation of the new industry, and chiefly the progressive imports and the rise in the rate of exchange which financiers seek in vain to reduce. The attempts to create new industries, and the help which the Government ought to give to these, especially at the commencement, will be more efficacious in reducing the rate of exchange than financial speculations. Industries will give work and bread, forthwith, to many poor people in the prosperous olive districts, but none the less poor in spite of that. Many other industries, anæmic up to now, would embrace this new industry, coming to give them an energetic push forward. How welcome it would be! The value of olive oil residuals is fully demonstrated. Its abundance is very great; it will be greater every day with the culture of the olive in new plantations. The pyroligneous products which can be extracted from it are of equal importance to those from wood. Notwithstanding the new industry, the cost of olive oil residuals for oil extraction will not increase, because use is now only made of 200 metric tons. By combining extraction with carbonisation, the cost price can only be less, and that of the pyroligneous products also. The cost price of methyl alcohol and acetic acid from olive oil residuals is one-fourth of that extracted from wood.

The consumption of pyroligneous products, which increases in every country, increases also in Spain. Methyl alcohol is

destined to be the most important of the products, owing to the industrial applications of grain alcohol, and of the new industries which use methylic alcohol. The exploitation of pyro-ligneous products once increased, its use in Spain would be profitable, looking to the cost price of alcohol and acid from olive oil residuals. The creation of this new industry will increase the value of oil products. Manufacturers have a very lucrative road to a great future. The financiers of this enterprise, worthy of great initiative, can make of it a national industry. If Spain aspires to sustain its credit abroad, if it be desired to lower the rate of exchange, it is necessary to create new industries like this, which utilises the abundant raw materials and which after a little would increase her exports. Spain, in spite of everything, must follow the indefatigable march of progress; she must exploit this industry herself before others come to do it.

Vladimir Guerrero patented in September, 1905, a process by which he obtained the products derived from the distillation of olive oil residuals by two processes, separate or combined. The first is supplementary to the extraction of oil from the residuals, the second is for making chemical products by treating the ammoniacal liquor.

TABLE XXXIV.—PRODUCTS OBTAINED BY DISTILLATION OF 1 TON OF OLIVE OIL RESIDUALS AND THEIR VALUE

Products from Residuals.	Products from Ammoniacal Liquor.
Yield per ton :—	Minimum yield per cub. m. (220 gals.) :—
Granulated charcoal, 25 per cent. 11	Ammonium sulphate, 3·2 per cent. 14
Tar special, 3 per cent. . . . 6	Methyl alcohol, 1·6 per cent. . 20
Ammoniacal liquor, 50 per cent. 10	Acetic acid, 2·5 per cent. . . 36
—	—
Pesetas . . . . . 27	Pesetas . . . . . 70
At the rate of exchange 30 per cent., francs 20·75 (or 16s. 8d.).	At the rate of exchange 30 per cent., francs 53·85 (say 42s. 10d., or 2½d. per gal.).
Rich gas (light or power) : 160 cubic metres which produce 10 h.p. effective hour which, at 5 centimes each, re- presents 12 pesetas or 9·20 francs extra (7s. 4d.).	

These results are the fruit of three years' experiments made with a demonstration plant situated at Cordova, where Guerrero placed himself at the disposal of manufacturers interested in his process and for which he was in a position to guarantee the yields given above. It is pleasant to register such a success, which is a great step in advance for this industry, the experimental field of which is very wide.

# CHAPTER VII

## STATISTICS OF THE WOOD DISTILLATION INDUSTRY

The following statistics of the wood distillation industry are taken from the United States *Forest Service Reports* :—

TABLE XXXV.—HARDWOOD, CHIEFLY BEECH, BIRCH, AND MAPLE

	1906.	1907.	1908.	1909.
Number of Establishments	86	100	101	—
Quantity distilled, cords	1,144,896	1,219,771	878,632	1,149,847
Cost	\$3,716,423	3,824,669	2,710,745	3,818,282
Products, Total Value	\$ —	7,661,379	5,408,265	7,641,690
Charcoal, bushels	45,657,721	50,772,234	37,286,520	53,075,102
Value	\$2,965,940	3,838,392	2,644,923	3,299,002
Wine alcohol, gals.	7,871,494	7,741,645	6,285,678	8,468,083
Value	\$2,676,191	1,153,307	1,084,223	2,082,253
Acetic acid, lb.	96,376,497	133,374,941	106,098,846	148,769,479
Value	\$2,017,331	2,565,938	1,636,825	2,202,847
Wood acetate, lb.	6,960,933	8,152,848	1,586,441	2,156,907
Value	85,777	94,446	13,457	22,203
Wood acetate, gals.	—	—	262,989	302,624
Value	—	—	25,024	27,779
Wine, gals.	250,610	382,959	57,829	37,995
Value	\$19,877	9,296	3,813	3,082
Other products, Value	\$ —	—	—	4,524

TABLE XXXVI.—SOFTWOOD PINE

	1906.	1907.	1908.	1909.
Number of Establishments	33	31	30	31
Quantity distilled, cords	50,234	62,349	90,212	115,310
Cost	\$129,358	210,844	207,202	241,726
Products, Total Value	\$ —	534,802	491,161	686,794
Wine, gals.	503,427	654,711	505,800	682,702
Value	\$238,612	304,860	166,343	243,491
Charcoal, bushels	791,887	1,158,364	1,995,728	2,403,401
Value	\$129,358	102,411	186,616	210,017
Wine, gals.	125,008	391,916	304,979	323,226
Value	\$17,249	69,399	56,043	70,080
Wine, gals.	648,120	760,836	966,675	1,364,984
Value	\$64,368	58,132	81,349	104,671
Wine, gals.	305,000	—	8,100	4,850
Value	15,380	—	810	218
Other products, value	\$ —	—	—	58,317

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The quantity, value, and average price of wood alcohol exported from the United States is given in the *Forest Service Reports* as follows:—

TABLE XXXVII.

Year.	Quantity. Gals.	Value. \$.	Average Price per gal. \$.
1902	626,925	338,619	0.54
1903	833,629	452,892	0.54
1904	1,194,466	585,359	0.49
1905	1,097,451	603,385	0.55
1906	780,222	466,467	0.60
1907	2,150,311	862,819	0.40
1908	1,958,630	819,753	0.42
1909	1,100,495	383,788	0.35
1910	1,328,601	581,820	0.44

According to R. C. Palmer<sup>1</sup> the number of plants in operation in the United States for the distillation of hardwoods in which other products in addition to charcoal were produced were in 1880, 17; 1890, 53; 1900, 93; 1907, 100; 1909, 116; 1910, 117; 1911, 105. From these the products enumerated below were produced:—

TABLE XXXVIII.—CHARCOAL

Year.	Production. Bushels.	Value. \$.
1880 <sup>2</sup>	54,000,000	3,678,000
1890 <sup>2</sup>	67,000,000	4,523,000
1900	17,154,000	726,000
1906	45,657,000	2,966,000
1907	50,772,000	3,838,000
1908	37,286,000	2,644,000
1909	53,000,000	3,299,000
1910	56,000,000	3,762,000

The following quantities of charcoal were also produced for pig iron alone:—

TABLE XXXIX.

Year.	No. of Plants.	Value of Product. \$.
1900	183	1,134,000
1904	74	1,292,000
1910	76	872,000

<sup>1</sup> *Oil, Paint, and Drug Report*, March 9, 1914.

<sup>2</sup> The figures for 1880 and 1890 include charcoal from softwood and charcoal kilns producing no other products.

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TABLE XL.—CRUDE WOOD ALCOHOL

Year.	Gallons.	Value. \$.
1880	130,000 <sup>1</sup>	86,000
1890	1,116,075	688,000
1900	4,945,000	1,977,000
1906	7,871,494	2,676,191
1907	7,741,645	1,153,307
1908	6,285,678	1,084,223
1909	8,468,083	2,082,253
1910	8,691,525	2,226,768
1912	9,500,000 <sup>1</sup>	2,660,000 <sup>1</sup>

TABLE XLI.—ACETIC ACID

Year.	Production. Lb.	Value. \$.	Proportion of Acetate for Acetic Acid, per cent.
1900	26,660,000	427,000	25
1904	27,001,000	537,000	25
1909	51,963,000	1,136,000	27

TABLE XLII.—ACETATE OF LIME

Year.	Lb.	Value. \$.
1880	6,593,000	156,000
1890	26,000,000	315,000
1900	86,826,000	981,000
1906	96,376,000	2,017,000
1907	133,375,000	2,566,000
1908	106,099,000	1,636,000
1909	148,769,000	2,203,000
1910	152,772,000	2,467,000

TABLE XLIII.—ACETONE

Year.	Lb.	Value. \$.	Proportion of Acetic Acid for Acetone, per cent.
1900	1,638,715	178,000	10
1904	1,300,000	161,000	8
1909	6,928,000	719,000	23

At a recent convention of Canadian chemists at Ottawa, it was stated that the capacity of the wood carbonising plants in

<sup>1</sup> Estimated.



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operation in Canada was equal to 500 cords, or 1000 tons of hardwood per twenty-four hours, and that the annual production of wood distillation products amounted to 75,000 tons of charcoal, 13,000 tons of acetate of lime, and 1,250,000 gallons of methyl alcohol. Other derivatives which are manufactured include, acetone oils, formaldehyde, acetic anhydride, methyl acetate, and sodium acetate.<sup>1</sup>

The retorts employed in Canada are long horizontal ones holding six cords of wood on the American principle, and the usual practice is followed with regard to the distillates. Part of the methyl alcohol is converted into formaldehyde. Four companies have a total capital of \$5,965,000 and employ about 2300 workmen. The output and value of the products being as follows:—<sup>2</sup>

TABLE XLIV.

Charcoal, 8,000,000 bushels of 20 lb.	\$560,000
Acetate of lime, 14,000 tons	465,000
Wood alcohol, 1,019,000 Imperial gallons	489,000
Acetone, 400 tons	110,000
Formaldehyde, 1400 barrels	50,000
	<hr/>
	\$1,674,000
Pig iron, 18,000 tons	325,000
	<hr/>
	\$1,999,000

With regard to the products of distillation, it is stated that The Standard Iron and Chemical Co. of Canada has an annual production of about 1,300,000 gallons of wood alcohol. The formaldehyde which is now manufactured in Canada is finding an extensive use as a smut preventive on corn. A new and extensive demand for the charcoal has now fortunately been created by the new nickel refining plants which are now in operation.<sup>3</sup>

<sup>1</sup> *Can. Chem. Jour.*, June, 1918.

<sup>2</sup> *Jour. Soc. Chem. Indl.*, 1913, 554.

<sup>3</sup> *Ibid.*, 1918, 456, R.

## PART II

### THE MANUFACTURE AND TESTING OF TAN WOOD EXTRACTS AND THEIR UTILISATION IN MODERN TANNERIES

#### CHAPTER I

##### CHESTNUT EXTRACT

*General Properties of Chestnut Wood—The Percentage of Tannin—Present Price of the Wood in France and Corsica—Deafforestation Yield in Extract of Wood from different Sources—The Water to be used in the Diffusion or Maceration of Wood—The Juice and Various Extracts from Chestnut Wood—Composition and Analytical Table*

THE chestnut, *Castanea visca*, is a tree of the Order Cupuliferae ; it grows in Savoy, Auvergne, Périgord, Provence, Brittany, Corsica, to a small extent in the North of Spain, in Italy, and also in America, but, as will be shown, is everywhere becoming scarcer. Chestnut wood has a certain amount of importance from the point of view of its tannin content. It was Michel of Lyons who discovered, in 1818, the presence of tannin in the chestnut-tree ; it was he, also, who suggested its use for the tanning of heavy leather. Chestnut wood intended for tanning, or for the manufacture of extracts for tanneries, should contain neither rotten wood, nor wood dead upon the tree, nor branches of less than 4 inches diameter at the small end, nor running roots. These restrictions do not apply to chestnut wood intended for the manufacture of extracts or gallic acid for dyeing. The cubic metre or stère of dry chestnut wood weighs 340 to 385 kilogrammes. The authors draw the attention of manufacturers of wood extracts and tanners, consumers of chestnut wood (which brings during the tanning of leather its contingent of pectic, resinoid, and amylaceous matters favourable to a good yield) to the importance of always requiring from the suppliers deliveries of sound chestnut wood and rejecting rigorously rotten or ferruginous rotten wood, as incapable of a normal yield, or only taking delivery of it at a considerable reduction in

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price. This damaged wood is only capable of being used for the manufacture of "gallic" acid for dyeing, the decolorisation of the liquor from the maceration of this rotten wood being difficult and costly.

TABLE I.—ANALYSIS OF SOUND AND UNSOUND CHESTNUT WOOD FROM VARIOUS SOURCES

	Gard (Southern France).		Lyonnais and Dauphiné.	
	Sound, per cent.	Rotten, per cent.	Sound, per cent.	Rotten, per cent.
Tannin, soluble . . .	7.40	2.80	6.10	3.40
Non-tannin . . .	1.90	1.10	1.50	1.00
Water . . .	54.25	63.28	53.20	64.24
Woody fibre . . .	36.45	32.82	39.20	31.36
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Total soluble . . .	100.00 9.30	100.00 3.9	100.00 7.60	100.00 4.4

The effect of the rotting of wood is to render insoluble a large proportion of the substances originally soluble. As to the price of chestnut wood, it has done nothing but increase for the last five years, for reasons to be explained later. In 1900 the extractors of the South of France and of Ardèche were already paying 14 to 15 francs (11s. to 12s.) the metric ton on the spot; at the present time (1908) they are paying 17 to 18 francs (13s. 7d. to 14s. 4d.). The price will go up still further as the chestnut plantations disappear daily and the country labourer is obliged to go farther afield to fell the trees, even to localities where the cost of felling, etc., of the metric ton of wood rises from 2 to 5 francs (from 1s. 6d. to 4s.). In Corsica the extractor buys chestnut wood by the stère (about 460 kilogrammes = 1012 lb.) at the rate of 9½ francs, or more than 20 francs (16s.) the ton. The freshly felled wood contains 68 per cent. of water; the green wood, three months after felling, contains 55 per cent.; the peeled wood 40 to 45 per cent. The wood is generally piled in stacks of 200 to 500 tons to dry, and the stock for consumption is made up from year to year. It loses on an average after that lapse of time 20 per cent. of water, and then only contains 33 to 35 per cent. The green wood of the chestnut-tree, with 75 per cent. of water, contains 4 per cent. of tannin on the trunk; ordinary wood, with 40 per cent. water, contains 6 per cent., and perfectly dry wood 8 per cent. Chestnut roots contain 7 per cent. of tannin; the bark 3 per cent. (17 per cent., Perkin and Everest). During the drying of the chestnut wood a portion

of the tannin resinifies. The northern chestnut wood is less rich than that of the south, and that of the west poorer than that of the east. The Corsican chestnut wood contains on an average 10 per cent. of tannin. Chestnut wood yields 4.74 to 5.71 per cent. of ash containing 70 to 80 per cent. of lime, 5 per cent. of potash and 4 per cent. of phosphoric acid. Its density is 0.588. The interesting question at the present time, and one which should engage the serious attention of the extract manufacturer and the large number of country folk in whose life the chestnut plays an important part, is the reafforestation of the chestnut plantations which have already disappeared and those which will rapidly disappear. The numerous extract factories are as heedless of their future supply as the peasants, who fell the chestnuts, without concerning themselves about the future and who only see in this felling the source of present gain.

*The Disappearance of the Chestnut-tree in France. The Cause and its Remedy.*—During the discussion on the French budget of 1904 the Hon. M. Pedebidou on two occasions drew the attention of the Minister of Agriculture to the disappearance of the chestnut-tree and asked the Government to take steps to remedy such a disastrous situation. "The disappearance of the chestnut-tree is exerting a most vexatious influence on the regular flow of streams of water. The denudation of the slopes induces torrents, with injurious results to the navigation of rivers." But that is not all. The chestnut-tree is a very precious tree, the culture of which represents a valuable source of profit to many departments. In addition to its fruit, which constitutes an important article of food, it yields wood for making vine props and the hoops and staves of casks.

By trituration, it yields tannic extracts, the use of which is becoming more and more general. Essentially a hardy tree, the chestnut-tree adapts itself to the most intractable soils.<sup>1</sup> Its disappearance would constitute a real disaster. Grave uneasiness, therefore, is produced by the crisis through which this tree is passing. An inquiry was made by the Department of Rivers and Forests (*Eaux et Forêts*) on the cause of the destruction and the means of remedying it. The following are the conclusions:—

The causes of the destruction of the chestnut are of two kinds: (1) The first consists in the chestnut disease, which assumes two distinct forms. One is the disease of exhaustion or decrepitude, which prevails in a great number of chestnut plantations, where the trees are old, because the cultivators impoverish them by stripping off their green leaves, the only

<sup>1</sup> Chatin (Ad.), "Le Châtaignier, Étude sur les Terrains qui Conviennent à sa Culture," *Bull. de la Soc. Bot.*, p. 198, 1870.

manure for the soil, and mutilate them by breaking and carrying away the branches, so as to procure wood for fuel and leaves for cattle-feeding. This disease is by no means of an epidemic nature, and attacks individual trees. To remedy it, all that has to be done is to stop the practices which occasion it, to preserve carefully the dead covering of the soil, to restrict the abuse of pasturage, and to manage and exploit the chestnut in a rational manner, felling the old and replacing them by young trees. The second disease, which is the real chestnut disease, the ink or foot,<sup>1</sup> attacks all trees without distinction, young and old, vigorous or decrepit. It has a decidedly epidemic character, which has earned for it the title of phylloxera in certain districts. The seat of this disease is in the roots, and its origin is due to a new parasitical fungus, the *Nyctophagus castanæ*. This disease has been reported from twenty-seven departments, in ten of which it has not made any considerable ravages as yet; eight showed depredations of less than 50 hectares (125 acres); in the following five, Dordogne, Gard, Ille-et-Vilaine, Morbihan, Lot, the area oscillates between 200 and 500 hectares (500 to 1250 acres). Finally, the devastation does not reach 1000 hectares (2500 acres) in the Haut-Pyrenees, but it exceeds this figure in the Basses-Pyrenees, La Corrèze and La Haute-Vienne.<sup>2</sup> The devastated area amounts to about 10,000 hectares (25,000 acres) on a total area of 350,000 to 380,000 hectares (875,000 to 950,000 acres), not including the chestnut-tree coppices, about 100,000 hectares (250,000 acres). No economical and practical method has been found for coping with this disease; the only way of preventing the spread of the disease is to pull up the trees attacked. The chestnut-tree is liable to two other diseases, the jaundice and the quittor (*le javart*),<sup>3</sup> but happily these diseases are not widespread and rarely cause the death of infected trees.

(2) The most important cause of destruction consists in felling the chestnut-trees for the manufacture of tannic acid extracts. The use of tannic extracts tends to replace that of oak bark in tanning to an ever-increasing extent. Chestnut wood, the percentage of tannin in which is 4 to 8 per cent., yields in France the largest quantity of these extracts. In view of this new outlet, which enables this wood to command remunerative prices, landowners, for the sake of immediate gain, do not hesitate to fell immature chestnut-trees. They

<sup>1</sup> De Seynes (J.), "De la Maladie des Châtaigniers appelée Maladie de l'encre," *Comice Agricole de l'Arrondissement du Vigan*, September, 1889.

<sup>2</sup> Delacroix, "La Maladie des Châtaigniers en France," *Bull. de la Soc. Mycol. de France*, t. xiii., 4 fasc., 1897.

<sup>3</sup> Prilleux (Ed.), "La Maladie des Châtaigniers dite le Javart," *Journ. d'Agric. Pract.*, p. 139, 1893.

are encouraged in their work of destruction by a large number of factories for the manufacture of tannic acid extracts, which have been established in numerous districts, the needs of which are always increasing. It is, more especially, within the last twelve years that these factories have multiplied rapidly. In 1875 there were only seven, at the present day there are in France twenty-six factories exploiting the chestnut-tree for the extraction of tannic acid. To these factories must be added those of Geneva (Switzerland), which are supplied, for the most part, with French wood. The actual consumption of chestnut wood by these twenty-six factories may be estimated at 450,000 metric tons, producing extracts of a value of 22,000,000 to 24,000,000 francs (£880,000 to £960,000). The hectare of chestnut-trees bears on an average a hundred trees (about forty trees to the acre), which may yield 375 tons of wood (150 tons to the acre); it will thus be seen that the consumption of chestnut wood by the tannic acid extract factories represents the disappearance of 1200 hectares (3000 acres) of chestnut-trees annually. This destruction is particularly intensive in Corsica, where it amounts to 200 hectares (500 acres) annually. In each of the departments of Gard, Lot, Dordogne, Corrèze, Haut-Vienne, De la Creuse, and D'Ille-et-Vilaine, the area from which the chestnut has been felled now exceeds 1000 hectares (2500 acres); it is 500 to 1000 hectares (1250 to 2500 acres) in the Basses-Pyrenees, La Lozère,<sup>1</sup> Saône-et-Loire, Loire Inférieure, Morbihan, and the Côtes-du-Nord.<sup>2</sup> Finally, it amounts to 200 hectares (500 acres) in La Sarthe, L'Allier, Le Rhone, L'Isere, La Savoie, La Haute-Savoie, and the Hautes-Pyrenees. Against the improvidence of the proprietors, which leads to this disastrous state of affairs, the Government is powerless. No legislative enactment can limit the right of the proprietor to use and abuse his chestnut plantations, except in very rare cases, provided for by the law relating to the reclamation of waste land. But the duty of the Government is to enlighten the rural population as to the gravity of the situation, and to make them understand the interest which they have in preserving and rationally exploiting the chestnut-trees. Formal instructions have been addressed to prefects, the agents of the Department of Rivers and Forests, and the professors of agriculture, that they use all the means in their power to promulgate in country districts notions of prudence and wise foresight on this subject. On the other hand, where the destruction is already consummated, the

<sup>1</sup> Crié, "Rapport sur les Maladies des Châtaigniers dans les Cevennes," *Bull. du Minist. de l'Agric.*, No. 7, an xiv, October, 1895.

<sup>2</sup> "Rapport sur les Maladies des Châtaigniers en Bretagne," *Bull. du Minist. de l'Agric.*, No. 8, 1894.

replanting of the chestnut woods is to be encouraged. With this end in view, measures have been taken to award medals and prizes at the agricultural shows, so as to recompense work of this nature. Whilst approving the initiative taken by the Forest administration, in view of the systematic destruction of chestnut-trees for tannic acid extracts, more radical measures may be necessary to circumscribe or limit this destruction. Would not the best method of inducing proprietors to replant their chestnut woods be to award them a bounty, which would be debited against the factories themselves? It would suffice for that purpose to place a special tax, which need not be very high, on tannic acid extracts, produced by the twenty-six factories already in existence. Nevertheless, so as to safeguard to a certain extent the interest of the tanner, and the very prosperous industries connected therewith, there would seem to be occasion to put a higher tax on foreign products imported for use in the tannery. A Bill, brought before the French Parliament on 6th July, 1889, by Dunaine and Hubert, complied to a certain extent with that object, since it tended to modify the general tariff of the French customs in regard to dye woods of foreign origin (quebracho and other woods). That Bill has never been discussed. But the attention of those interested is drawn to it. Again, as regards Corsica, a lecture of September 9, 1901, on "The Felling of Chestnut-trees in Corsica," by Donati, special Professor of Agriculture at Bastia, goes thoroughly to the root of the question. He said:—

"The question which I have to discuss before you is assuredly the most important of all those which concern not only the rural economy but the whole well-being of Corsica. The destruction of chestnut-tree plantations by contractors who supply the tannic acid factories is pursued under such conditions that we consider it our duty to make known not only the advantages which the culture of the chestnut presents for our people, but also the causes of this deafforestation and its immediate consequences, not only from the point of view of food supply, but also as regards the climatology and the future of agriculture. These trees, which cover 30,000 hectares (75,000 acres) on the hill slopes, have always played an important rôle in all the critical periods of the history of Corsica; at the time when the people fought for their independence, they procured the means of existence from these trees; even at the present day, when misery extends its ravages farther and farther into the country districts, they constitute the principal resource of those farmers who have given up the cultivation of the soil. By its richness in nutritive elements, the flour of the chestnut forms a complete food. The recent analyses by Balland (*Pharmacien Principal de Première Classe*) afford very precise data on this

point: a quantity of chestnuts from Piedmont, which are those most resembling Corsican chestnuts, gave, on analysis, the following figures: albuminoids 5.98, fat 3.78, sugar and starch 86.82 per cent. If we compare these figures with the analysis of Dattel wheat, which is grown very widely, an analysis which is also given by Balland, it will be surprising to see how great the analogy is between these two products: albuminoids 10.53, fat 1.44, sugars and starch 84.28 per cent. The percentage of nutritive elements in chestnut approaches very near to that of wheat, and this explains how our highland population from time immemorial have been able to nourish themselves almost exclusively on soup and cakes made from chestnut flour. That shows us also the great benefit which may be drawn from these fruits in grave circumstances for the feeding of towns and villages. Chestnut wood is not less precious for domestic uses; exploited as coppices of five to six years old, it is used to make baskets, forks, whip-handles, tool-handles; it is used like the nettle-tree (*micocoulier*) and the willow (*osier*) in the south of France; as it grows larger it is used as vine props and as wood for fences; used for carpentry purposes, it equals oak in durability; transformed into beams, planks, and boards it is used for all the purposes of coach and waggon-building, cabinet-making, etc., and even exposed to the wind, sun, and rain, without being protected by any coating, its durability is unlimited; split up into staves it is used to make excellent barrels, of all dimensions, for the storing of wine. As dead or withered wood it is equally useful, for it is an excellent firewood for ovens as well as for heating apartments. The care required for the growth and management of these trees as well as for the collection of the fruits is almost *nil*. Generally the tree is a wild one—seven to eight years old—which has come up naturally and been grafted on the spot; it grows as well as it can, surrounded by brushwood, until it commences to bear seed about the fifteenth or the twentieth year. The brushwood is then cleared away all round the plant, and after that the ground is cleared every year to allow the chestnuts to be collected. A chestnut may attain very great dimensions; many are met with which measure 6 and 7 metres (20 to 22 feet) in circumference and 25 to 30 metres (80 to 120 feet) in height. The value of these trees is based on their dimensions and the quality of their fruit; it varies from twenty to fifty francs (16s. to £2); some are worth more than a hundred francs (£4), but these are exceptional. The yield per foot easily reaches 10 to 12 per cent. of this sum. The collection of the nuts is done, generally, by the proprietors themselves, and in that case it entails no great expense, because, with the exception of clearing away the brushwood and moss, which is done by men in their spare time, the nuts are gathered



by women and children. When the landowners engage work-people for the whole nut harvest they are paid in kind, say one-third or one-half. They, on their part, are bound over to proceed in the beginning of September with the clearing of the chestnut woods, to split up and carry the wood intended to feed the drying kilns, collect the nuts, carry them to the kilns, and dry them. The harvest requires about two months' work; it commences from the 15th to the 20th of October and finishes about the end of November; decortication is proceeded with as soon as the nuts are sufficiently dry to be brought to the mill. There is reason, therefore, to say that the chestnut is a most important tree; and the void which the disappearance of these trees will create in country districts will be irreparable. The effect of this felling on the climate of the country will not be less disastrous. At the present time it pleases every one to extol the climate of Corsica. The town of Ajaccio owes to it the favour which it enjoys as a winter resort, but it is greatly to be feared that this will not be so when the slopes of the mountains are stripped, because it is recognised that it is the forests and the woods which render climates more genial, less variable, and more constant. On the other hand, the influence of these forests is intimately connected with the prosperity of agriculture. They regulate the flow of torrents; they retard the melting of the snow, and the water penetrating into the soil converts it into huge reservoirs yielding their overflow to the rivers even during summer as required. Hence the regularity in flow of rivers rising in wooded districts, whilst on bare ground the water rolls on in torrents carrying sand and gravel in its train, giving rise in the plains to floods which devastate the harvest and make considerable ravages. Besides the torrents from the hillsides are very abundant in winter and dry up in the heat of summer. The farmers of the *arrondissement* of Bastia have already had a foretaste of what is in store for them, on the night of the 4th August, 1899, when the waters of the rivers Alesani, Fiumalto, Golo, and Bevinco overflowed their beds, and did considerable damage. These recent inundations cannot, it is true, be imputed to tree felling; but these catastrophes, which up to now only recur at somewhat long intervals, will become more frequent owing to the destruction of the chestnut plantations. These facts have, moreover, been verified as regards the large rivers of France: the Rhone, the Loire, the Rhine, the most disastrous floods on which have been attributed to the felling of the trees on the mountains.<sup>1</sup> It would be unfortunate if the people of Corsica, already so tried by the economical crisis,

<sup>1</sup> The inundations of October 16 and 18, after the Congress, and produced not by the overflow of the rivers but by torrents from deafforested tracts, have shown how well founded were our apprehensions.—F. D.

which presses more heavily on that country than elsewhere, had also to undergo, in their turn, this sad trial, the immediate consequence of which would be the abandonment of the low grounds formed by the alluvium of the rivers; these soils being the most fertile and the only ones whose cultivation is still remunerative. There is an equally important point of view, which it is permissible to glance at, that is, the possibility of Corsica being left to its own resources alone. Quite a recent experience, a simple strike of porters,<sup>1</sup> risked placing the people at their last resource. What would happen in time of war if this country were deprived for long months of outside imports? We are told that the War Department, as a precautionary measure, takes care to provide stores. Would it not be preferable to preserve to Corsica its own crops, like the chestnut-trees, which are at the door of every family and the fruits of which can, in grave circumstances, suffice for the primary needs of the people? No one can contest the gravity of this felling. It is true that in certain localities they have rested content with thinning the chestnut plantations, and that, on the other hand, the stocks still remain in the ground, but the bare tracts are already numerous, their area increases from day to day, and the consecutive misery of bad harvests aiding the contractors, it is easy to foresee the date when this deforestation will be complete. The two factories which extract gallic acid, or chestnut extract for tannery purposes, from chestnut-tree wood and which at present exist in the arrondissement of Bastia, absorb 140 tons of wood a day, corresponding to thirty or forty plants, say almost a hectare of chestnut-trees. To that must be added the wood which is exported and that which will be absorbed by a third factory in process of construction,<sup>2</sup> and it will be seen that in less than fifty years the chestnut-trees of Corsica will have succumbed. The Agricultural Societies and the General Council are troubled at this state of affairs, and have asked for exceptional measures for dealing with those proprietors who allow their plantations to be destroyed; but these solicitations struck against the rights of property and have had no result. It is urgent, however, to find a remedy for this state of affairs, whilst the interest of the proprietors and that of the public are at the same time reconciled. The chestnut woods on the hill slopes may be divided into two categories, those which have been felled and which are transformed into thickets, and those which are still intact. Nothing would be more simple than to cause the first to benefit by the law of 1860,<sup>3</sup> which renders planting obligatory on slopes and the summits of the mountains, exempting them from all taxes

<sup>1</sup> The Marseilles strike.

<sup>2</sup> Since 1901 two new factories are at work.

<sup>3</sup> Repealed by the law of April 4, 1882.

for thirty years.<sup>1</sup> This advantage would induce the proprietors themselves to solicit the transfer of their thickets to the forest regulations and to reconstitute their chestnut woods. They would preserve all their rights on the new plantations, except felling, which would be done under the control of the Forest Department. In regard to chestnut woods still in existence or in process of exploitation, and which it would be desirable to preserve, it would be advisable that these also should be put under the management of the forestry department, at the same time, we repeat, paying due respect to the rights of the proprietor. At the present day the contractors cut all the trees; all fall under the blind axe of the butcher, the youngest trunks as well as the very oldest, which they leave in great part on the ground as unsuitable for their industry, and these lands are afterwards given over to the inroads of cattle.

"The function of the forest agents would be to single out the trees to be preserved amongst the youngest and the very oldest, so as to render felling less damaging, from a foresting point of view, and to assure the replanting of the felled portions. In exchange for this right of control, the proprietors would benefit by exemption from taxes for thirty years. At the expiry of that time the State would still maintain its right, and the proprietors could only fell or make a clearance of their chestnut plantations in so far as the interests of arboriculture demanded. These measures are of an administrative nature. It will suffice to indicate them. There are others of an arboricultural order, which devolve more specially upon our functions, and the effect of which would be to oppose deafforestation on the slopes of the mountains by rendering the growth of the chestnut more profitable. It is a known fact that deafforestation has commenced, and is being actively pursued chiefly in localities where the cost of harvesting is the greatest, either owing to the poor quality of the chestnuts and their low price, or owing to want of labour. In those districts where chestnuts are sold in a fresh state, and where they yield good quality flour, proprietors do not rob themselves of their chestnut trees so readily, and contractors do little business there. If it were, therefore, possible to diminish the cost price whilst improving the quality of the product, it is certain that proprietors would forego their trees less readily. That is the problem which we have tried to solve, by modifying the system of drying in use which is a most defective one."

Confining ourselves to the subject of the chestnut only, it will be unnecessary to follow the author of this important communication further, but it may be added that it fully confirms

<sup>1</sup> Art. 226 du Code Forestier.

the present situation of the chestnut plantations in France, and with an Inspector of Rivers and Forests,<sup>1</sup> an authority on the subject, the authors enunciate the following thesis: *The chestnut-tree will disappear from France if the tannic acid extract industry continues to fire upon it with red-hot bullets.* This disappearance of the chestnut will be a great misfortune from a local point of view, regard being paid to the food of the peasants, and a disaster from a general point of view, by still further increasing the denuded surface of the mountains. Moreover, the disappearance of the chestnut will ruin the chestnut extract industry. There exist in France a considerable amount of coppice lands—individual and communal<sup>2</sup>—planted with oak and exploited at short intervals, the revenue of which amounts to nothing with the extremely low price of barks. These coppices, thinned at twenty years, reserving 300 standards per hectare (120 per acre), can at the next interval provide 300 oaks forty years old capable of yielding 50 tons of twisted trunks unfit for working, as the limestone of the south cannot elongate the stock of the oak, but, having grown bathed in sunlight, they are capable of supplying the extract factories.

On that account it would be advisable to substitute oak extract for chestnut extract. Now it is known that in tanneries, except for tanning sole leather (*lisse*), a properly manufactured oak extract would have, on the initiation of the Hungarian factories, a big outlet sufficient from the very beginning to keep several extract factories at work, which would then find themselves provided with oakwood, indefinitely, by applying the system of replanting indicated above. On the other hand, the tables prepared by Mangin in his tabulation of the statistics of 1902, show what is the actual quantity of chestnut trees in France, *viz.* 90,000 hectares (225,000 acres) in chestnut coppices, and 350,000 hectares (875,000 acres) in chestnut woods. If it be taken that on an average fifty chestnut trees represent 1 hectare of a chestnut plantation and that the average weight of a tree when exploited is about 2 tons, the total amount of chestnut trees in France will be represented by the formula: 350,000 hectares with 50 trees = 17,500,000 trees, or in kilogrammes, 17,500,000 trees at 2000 kilogrammes (2 metric tons) = 35,000,000,000 kilogrammes (35,000,000 metric tons). As the French extract factories (see Chapter IV.) consume annually 450,000,000 kilogrammes (450,000 metric tons) (certain factories work Sundays and holidays (*fêtes*), so it is necessary to calculate 500,000 tons as the annual consumption), the actual stock, which has just been estimated, will therefore be exhausted in  $35,000,000 \div 500,000 = 70$  years—that is supposing that this

<sup>1</sup> M. Teissier.<sup>2</sup> About 2,800,000 hectares (7,000,000 acres).

amount was available. Now a number of chestnut-trees are preserved as fruit-trees, others for some other reason, and finally others grow in spots where they cannot be reached; this quantity, which may be called a reserve factor, is difficult to estimate and disturbs the calculation of the longevity of the present factories. It would be easy to ensure this longevity by a little replanting, because it suffices, from the above figures, to replant fifty trees per hectare (twenty trees per acre) per annum; each tree grows 0.050 cubic metres annually (1500 kilogrammes per hectare, or 600 kilogrammes = 1320 lb. per acre); the 350,000 hectares (875,000 acres) could easily produce, without being impoverished, 525,000 tons per annum. To conclude, therefore, to maintain the present prosperity of extract factories, it will suffice if each large chestnut-tree felled be replaced by two young plants—that is a matter of 400,000 plants annually, which the State or departments should distribute gratuitously; an easy matter to organise. Finally, according to other estimations (on the Savoy) it will be necessary to allow for an annual average production of 4.6 cubic metres per hectare, or more than 900,000 tons per annum. In any case the remedy for the depletion of the chestnut plantations is easily applied, if regard be had to the preceding and if prompt and thorough action is taken against this deplorable state of affairs.

*Yield of Chestnut Wood.*—The yield of extract of 25° from chestnut wood evidently varies with the nature of the tree treated. It is also a factor of its state of hydration and of the district or place in which it has grown.<sup>1</sup> The wood of the South of France is richer than that of the North or even of Central France, likewise those of the same district but grown with a southern aspect are richer than those with a northern exposure. If it were practicably possible to select the trees according to these principles the tannin industry would gain considerably; unfortunately with the present method of felling it is not possible even to dream of it. It is necessary to take things as they come. The average yield of a well-installed and efficiently worked factory, in which the manufacture is controlled, may be estimated for 450 kilogrammes of chestnut wood with 40 per cent. moisture, that is to say, after a year in the shed, or 550 kilogrammes with 55 to 60 per cent. moisture, at 100 kilogrammes of extract at 25° B. This yield may be commercially assured, and that whether intensive working be adopted, that is to say, to obtain from a given installation a maximum production, or whether rational working be pursued, which consists in forcing the maximum yield, by first drawing off the quintes-

<sup>1</sup>Fliche and Grandeau, "On the Influence of the Chemical Composition of the Soil on the Growth of the Chestnut," *Ann. de. Chim. et de Phys.*, 5e Series, vol. iii., 1876.

sence of the juice contained in the decantation mud (by the authors' processes described later) and by a more methodical extraction of the wood in autoclaves or in the open air. In principle, the authors recommend this rational method because it realises greater profit than that yielded by the intensive method, which leaves too much to be desired, from the point of view of extraction and the percentage of tannic acid in the product. Several factories have already adopted the rational method, which, although producing less than the intensive method with equal capacity of plant, yet yields a very liberal compensation in the amount, quality, and strength of the extract obtained, from a given weight of wood.

TABLE II.—SHOWING THE DIFFERENT YIELDS OF CHESTNUT-TREES BY THE RATIONAL METHOD OF TANNIN EXTRACTION

50 per cent. Lyonnais. " " Dauphiné.	Dry Branches.	Green Branches.	Dry Roots.	Fresh Roots.	Roots and Branches.	Stripped Wood.	Corsean Stripped Wood.	Cord Stripped Wood.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Yield from wood of 20° extract per cent. .	31.7	31.5	39.0	42.0	35.9	35.0	44.0	32.5
Yield from wood of 25° extract per cent. .	24.8	24.0	31.0	33.0	28.0	28.0	35.0	26.0

All these tests were made on a minimum quantity of 20 tons of wood or roots, using maceration by seven washings and recuperation of the mud, according to the authors' system. The pressure in boiling was uniform in all the tests, that is to say, 1.5 kilogrammes maximum for all the boilings. The strength of the liquors varied from 4.3° to 5° B.

*The Influence of the Water used for Diffusion of Wood and Bark.*—The importance of this question being granted, the authoritative work on the subject by Ed. Nihoul, director of the Tanning School of Liège, on the influence of the water used in the maceration or the extraction of tannin from wood or bark in the tannin industry or in tanneries, is worthy of due consideration, and the authors do not hesitate to publish it *in extenso*, especially since it plainly confirms the industrial results obtained by the authors in this special tannin industry.

*Note on the Transformations which are Produced in the Infusion of Tanning Materials.* By Ed. Nihoul and L. van de

Putte.<sup>1</sup>—In a previous research<sup>2</sup> we have shown that the loss in tannin produced during the extraction of tanning materials by saline solutions was most often independent of any increase in insoluble matter. In other words, it is not owing to the formation of insoluble tannates that there is a diminution of assimilable matter by hide powder in the conditions incidental to the analysis of tannins. We found that these losses arise, partially or wholly, from the transformation of the tannin into non-tannin, the latter remaining in solution in the infusion, passing through the filter of hide powder without being absorbed. In some cases, however, there is manifestly produced a precipitate of a tannate of an alkaline earth which certainly greatly increases the loss. On the other hand, we have determined that more often the originally bright infusions obtained become turbid somewhat rapidly after filtration, even infusions obtained by the use of distilled water. The fact is not new, however, as far as the last point is concerned. Dr. Paessler even attributes to these precipitates, which eventually form in tannin liquors intended for analysis, the errors in the tannin obtained, when the last portions of the liquid which pass through the filter are used for the determination of the total extract.<sup>3</sup> When extracting is done in the factory for the manufacture of the liquor, distilled water is not employed, the tannery water, generally well water, and consequently charged with mineral matter, being employed. There would be nothing impossible, therefore, in that case, if the substances in solution should interact to modify the solubility of these slightly soluble tannins, to which Paessler attributes the precipitation phenomena produced in the infusions intended for analysis. In the case of hard waters the precipitate is peculiarly abundant, and occurs very rapidly after filtration. We endeavoured to ascertain whether the deposit thus formed was due to matters assimilable by the skin, and, if so, what were the losses of tannin caused by this factor in the liquor. The importance of the question will be realised, for should this be the case the phenomenon would result in a still further increase in the loss of tannin mentioned in our previous research. In fact, from the rapidity of precipitation it would seem that the greater part of these insoluble tannins escape the action of the hide, and are deposited at the bottom of the vats or on the surface of the leather without penetrating into it. The examination of this question led us to try and ascertain, first of all, what happens when the

<sup>1</sup> Communication to the Liège Section at its meeting on November 12, 1903.

<sup>2</sup> E. Nihoul and L. van de Putte, "Effect of the Chlorides and Sulphates of Natural Waters on the Extraction of Tanning Substances," *Bull. Assoc. Bel. des Chimistes*, 1903, Nos. 8, 9, and 10, pp. 298 *et seq.*

<sup>3</sup> *Deutsche Gerber Zeitung*, 1901, No. 132 to 142; *Bull. Assoc. Bel. des Chimistes*, 1904, pp. 115-123.

extraction is performed with distilled water, and we have been able to discover a much more important cause than that found by our colleague, Dr. Paessler, of the loss of tannin which tannin infusions undergo after being preserved for some time. The results of this research are now given, reserving for future publication our practical tests with tannery waters. Three commercial tanning materials—oak bark, pine bark, and sumac—were analysed by the method of the International Association of Leather Chemists and gave the composition embodied in Column I. of the following tables:—

TABLE III.—EXPERIMENTS ON THE EXTRACTION OF TANNING MATERIAL USING DISTILLED WATER AS A SOLVENT. OAK BARK

[illegible]

TABLE IV.—EXPERIMENTS ON PINE BARK

[illegible]



TABLE V.—EXPERIMENTS ON SUMAC

	I. Normal Infusion.	II. Same diluted one-half.		III. Same after three days.		IV. Same plus Thymol.		V. Same Sterilised.	
			D.		D.		D.		D.
Extract total . . .	35.54	34.83	- 0.71	35.32	- 0.22	35.14	- 0.40	35.25	- 0.29
" ash . . .	2.50	2.47	- 0.03	2.54	+ 0.04	2.63	+ 0.13	2.93	+ 0.43
" organic . . .	33.04	32.36	- 0.68	32.78	- 0.26	32.51	- 0.53	32.32	- 0.72
Non-tannin total . .	16.63	16.80	+ 0.17	17.91	+ 1.28	17.21	+ 0.58	17.64	+ 1.01
" ash . . .	2.46	2.35	- 0.11	2.48	+ 0.02	2.48	+ 0.02	2.66	+ 0.20
" organic . . .	14.17	14.45	+ 0.28	15.43	+ 1.26	14.73	+ 0.56	14.98	+ 0.81
Total matter fixed by skin . . .	18.91	18.03	- 0.88	17.41	- 1.50	17.93	- 0.98	17.61	- 1.30
Mineral matter fixed by skin . . .	0.04	0.12	+ 0.88	0.06	+ 0.02	0.15	+ 0.11	0.27	+ 0.23
Tannin . . .	18.87	17.91	- 0.96	17.35	- 1.52	17.78	- 1.09	17.34	- 1.53
Water . . .	8.67	...	...	...	...	...	...	...	...
Insoluble . . .	55.79	...	...	...	...	...	...	...	...

The tanning substances in these three raw materials were afterwards extracted in Koch's apparatus,<sup>1</sup> using distilled water and working on 27 grammes of oak bark, 17.8 grammes of pine bark, and 17.5 grammes of sumac respectively. The last portions of the infusion were concentrated so as to obtain 1 litre of infusion with each substance. The solutions were then filtered so as to obtain limpid filtrates, and the first 100 c.c. which passed through was rejected in each case so as to avoid the errors occasioned by the absorption of tannin by the filter paper. From the remainder, after rendering the bulk homogeneous, four portions of 150 c.c. were drawn and treated as follows: To the first 150 c.c. of distilled water was added and the mixture analysed; the figures given in Column II. were obtained in that way. To the second 150 c.c. of distilled water was likewise added, but the mixture was not analysed until three days afterwards. The results are given in Column III. To the third part of the infusion 150 c.c. of distilled water was likewise added and preserved for three days before being analysed, but a small piece of thymol was added to the flask in the beginning to prevent fermentation; the figures obtained on analysis are given in Column IV. The fourth portion was likewise protected from ferments by sterilisation. The latter operation was conducted as follows: The liquid was run into a 300 c.c. graduated flask and 100 c.c. of distilled water added. The flask was closed by an asbestos plug, previously scorched by passage through a Bunsen burner. The content of the flask was brought to the

<sup>1</sup> Nihoul (Ed.), "Analysis of Tanning Substances and the Yield Obtained in Tanneries," *Bull. Scien. de l'Assoc. des Ecoles spéciales de Liège*, 1903, No. 2 et seq.

boiling-point on three succeeding days for two to three minutes. The third day distilled water was added to make up the bulk to 300 c.c. (Column V.). The first column gives the results of the analysis under the normal conditions of the International Association, whilst in the others the tannin solutions were diluted 1 to 1. A peculiar thing was that none of these solutions became turbid after three days' standing, from which it may be inferred that the deposits obtained hitherto are due to slightly soluble tannins, which in the present case are held in solution by the excess of solvent. Let us examine what takes place in the case of each tanning material.

*Oak Bark.*—The total extract has diminished from Column I. to Column II., and this diminution affects both the organic non-tannin and the tannin, the latter a little more so. This diminution is accentuated in Column III., but here the non-tannin is more especially affected, which shows that chemical changes are produced in the tanning liquor during the three days' standing of the solution. These changes do not occur in the presence of thymol, which would seem to indicate that they were due to micro-organisms; Column IV., in fact, shows barely appreciable losses. But the loss in tannin appears again in Column V., and even exceeds the loss undergone by the liquid left to itself for three days; it is almost 1 per cent.; however, the amount of non-tannin has increased by almost 0.50 per cent. This partial destruction of the tannin and increase of the non-tannin has been already established by Parker and Procter (*Journ. Soc. Chem. Ind.*, 1895, p. 635); it is due to the action of heat on the tannin solution. It is one of the chief factors which led to the method of extraction of the International Society of Leather Chemists. It is also found that the dissolved mineral matter is increased by allowing the tannin solution to stand in the flask. That increase being really due to the action of the infusion on the glass. The authors observed the same to occur in leather analysis.<sup>1</sup>

*Pine Bark.*—The loss in total extract and in organic extract, in the case of oak bark, is repeated in the case of the pine, but with greater intensity, and a peculiar thing is here noticed, that neither the solution to which thymol has been added (Column IV.) nor the sterilised solution escapes this loss. It would, therefore, be impossible in this case to explain the phenomenon by the intervention of lower organisms. The most appreciable losses in total extract and in organic extract occur in Columns III. and IV., and possibly diastatic action may be the cause of the change. The presence of diastases in the infusions is

<sup>1</sup> "Chemical Examination of Leather," *Revue Universelle des Mines*, etc., 1901-2, t. lvi.

possible in all cases, for the greater part of the infusions are obtained at a lower temperature than 50° C. (122° F.). The action of the heat necessary for sterilisation has similarly occasioned a loss in tannin and a gain in the non-tannin. As to the increase in the mineral matter, it is again found in the pine bark as it was in the oak bark.

*Sumac.*—This tannin shows a more passive behaviour than the preceding. In fact, the decrease in total extract and in organic matter is barely appreciable. It is under the action of heat (Column V., sterilised solution) that the product shows itself the most sensitive as regards organic extract. Here, as in the previous cases, the losses in tannin of the solutions to which thymol was added are less than those of similar solutions, the compositions of which are tabulated in Columns III. and V. As to the mineral matter, here it again increases and agrees with the duration of the contact with the glass flask and the temperature to which the infusion has been subjected. The general conclusions to be drawn from the experiments may be expressed as follows:—

(1) Dilution of the infusions intended for analysis injuriously affects the accuracy of the results, the total extract and the total organic extract being lower in dilute solutions. If Columns I. and II. be compared it will be seen that the loss in organic extract especially affects the tannin. It follows that the clause proposed by Professor Procter at the Paris Congress is perfectly justified. In order that the results obtained by different chemists may agree, it is indispensable that they should operate on infusions the tannin content of which is appreciably the same. Moreover, in two cases out of three it is only the tannin that is affected, the loss in organic extract being, even as regards the pine and the sumac, slightly lower than the loss in tannin. One might perhaps see in this fact a *direct action of water on the tanning substance*, which might be more easily entrained by the steam during evaporation, this actually occurring with certain non-volatile organic matters such as sugar and glycerine. Another influence may very probably intervene in these losses of tannin, the duration of filtration of the original infusion. Paessler found (*loc. cit.*), in fact, that in the filtration of tannin infusions the tannin determined in the filtrate after 400 to 500 c.c. had run through was somewhat less, owing to the precipitation of slightly soluble tannin. The loss sustained under this head, determined on the whole extract, is comparatively small, not amounting to more than 0·3 per cent. It even happens that certain tanning substances, such as the mangrove, undergo no loss under such conditions. It may again be asked whether the losses so sustained are due to the precipitation of slightly soluble tannins or to the phenomena indicated in preceding

researches. In any case, the differences in the losses of tannin, shown in Column II. on the one hand and in Columns III. and IV. on the other hand, show that precipitation can only account to a slight extent for the losses found.

(2) The precipitates which are sometimes formed in infusions when working by the rules of the International Association, which are dissolved on heating and are eventually reprecipitated on cooling, remain in solution when the amount of solvent is increased.

(3) A third conclusion to be drawn from these experiments is the necessity of immediately submitting tannin infusions to analysis, in order to avoid errors in the tannin determination. Analogous facts have just been observed by Paessler with juice obtained from myrobolam extract.<sup>1</sup> The explanation of this may perhaps be found in the fact that a tannic acid extract analysed at different intervals often yields slightly different results.

(4) Care must be taken not to heat too strongly during extraction. In our opinion it would be well if the International Association made the rules in this connection more precise. The foregoing considerations may be useful after noting the slight differences which have occurred in the German<sup>2</sup> section of the International Association regarding the analysis of tannic acid extracts.

*Action of Saline Matter on Tannin Infusions and Extracts.*

—The great importance to the tanner and to the manufacturer of tannic acid extracts of using only the purest possible water containing the smallest amount of saline matter has elsewhere been described.<sup>3</sup> For some years now the use of extracts for tanning has become so general in Belgium that several firms use such products alone, having ceased to employ oak bark and even tropical tannins. It will not, therefore, be uninteresting to try to find what may be the effect of tannery waters on solutions of tanning materials, the more so as this question will verify whether osmotic phenomena intervene in the loss of tannin indicated in a preceding research. The formation of more or less abundant precipitates, which form after some time in infusions obtained by the use of hard water, has already been pointed out.<sup>4</sup> The precipitation is more or less abundant and more or less rapid according to the amount of salts held in solution by the water. The following were the results obtained with sumac in the first research on this subject.<sup>5</sup> In the experi-

<sup>1</sup> "Ueber das Verhalten von Myrobolanen-extracten bei der Aufbewahrung unter Verschiedenen Verhältnissen," *Deutsche Gerber Zeitung*.

<sup>2</sup> *Collegium*, 1903, Nos. 70, 80, 81, and 82.

<sup>3</sup> *Bull. Assoc. Bel. des Chimistes*, 1903, Nos. 8, 9, 10.

<sup>4</sup> *Idem*, 1903, No. 11.

<sup>5</sup> *Collegium*, 1902, p. 89.

ments with sumac the liquid passed through turbid even when an extra strong filter, Schleicher and Schull's No. 605, was used. It was not until after 100 c.c. of liquid had run through that the liquid was fit to be used for the estimation of the non-tannin. Such phenomena are accentuated in the case of the waters V. and VI. With sumac, filtration was extremely difficult, and it was found that the liquid obtained bright by being passed through the extra strong filter No. 605, immediately became turbid to such an extent that it was necessary to refilter it through a second filter, through which it was passed twice. This fact explains the decrease in the total extract obtained by analysis. The tannery waters referred to gave a fixed residue of 842 milligrammes per litre for the first, 1843 and 2070·5 milligrammes for the two others, *i.e.* waters V. and VI. The losses on ignition, not including the carbonic acid, were in these cases only 76 and 37·5 milligrammes; the fixed residue therefore consisted almost entirely of mineral matter. The lime estimation gave respectively 276·4 and 458 milligrammes, the chlorine 395·5 milligrammes and 465·5 milligrammes, the sulphuric acid 270 and 338·3 milligrammes; the two waters both contained large amounts of calcium chloride. The precipitate formed in sumac infusions, obtained by means of these waters, was so abundant as to cause the organic extract to fall from 33·96 to 18·42 and the tannin from 23·02 to 2·11, evidently disastrous results for the tanner and which astonished the investigator himself. In his researches on the effect of chlorides and sulphates, the reappearance of these precipitates was noted although, owing to the small content of the solutions, they were formed only after some time, but, in actual practice, when these deposits consist of tanning material, they almost completely escape from the tanning, since they are deposited in the bottom of the baths or on the surface of the leather. Besides, it is necessary to ascertain whether chemical reactions, after a lapse of time, take place between the tanning material and the salts present, so as to lower the percentage of matter assimilable by hide powder. The following experiments were limited to testing the action of calcium chloride, sodium sulphate, and bicarbonate of magnesia. Accordingly, infusions of tanning materials were prepared in distilled water to a concentration double that of the normal concentration, that is to say of the concentration prescribed by the International Association of Leather Trades Chemists. As in previous cases the experiments were on oak, pine bark, and sumac. The litre of infusion was in each case divided into 250 c.c. To the first portion 250 c.c. of distilled water was added, to the second an equal volume of water containing 0·1 per cent. of calcium chloride, to the third the same volume of a 0·1 per cent. solution of sodium sulphate, to the fourth also an equal volume of a 0·1 per cent. solution of bicarbonate of magnesia. The first vessel

therefore contained an infusion in distilled water brought to the normal degree of concentration, the second a normal infusion in water containing 0.05 per cent. of calcium chloride, the third likewise in water containing 0.05 per cent. of sulphate of soda, and finally in the fourth the tanning material was present in a solution containing magnesium bicarbonate in the proportion of 0.05 per cent. The liquids, thus brought to the right degree of concentration required for analysis, were left in closed flasks exposed to the light for three days in presence of thymol, then filtered and analysed by the method of the International Association of Leather Trades Chemists. The same experiments were repeated with commercial tannic acid extracts. Quebracho extract, chestnut extract, and mimosa extract D were tested in this way. Columns I. of the following tables show the results of the analysis of the normal infusion; Columns II. correspond to the calcium chloride solutions; Columns III. to the sulphate of soda, and Columns IV. to the bicarbonate of magnesia. Among the three saline matters used two of them lose weight on ignition; it follows, therefore, that the mineral matters found in the ash, whether of the total extract or of the non-tannin in these cases, will be less than those which go to increase the percentage of total extract and of non-tannin. It is thus, for example, that in the total extract the chloride of calcium is recovered with its six molecules of water of crystallisation, whilst anhydrous calcium chloride is found in the ash of that extract. This would lead in the ordinary calculation of the results to a fictitious increase in the organic extract. It must not, however, be forgotten that this cause of error reappears in the determination of the non-tannin and its ash. That is why it was not taken into account in our previous researches. Sodium sulphate loses its water of crystallisation at  $100^{\circ}\text{C}$ . ( $212^{\circ}\text{F}$ ). Now as the total extract and the non-tannin are dried at  $105^{\circ}\text{C}$ . ( $221^{\circ}\text{F}$ ), this salt ought to be recovered integrally in the ash. As to magnesium bicarbonate, it apparently should be converted completely into neutral carbonate by evaporation of its solution and into oxide by calcination. It was, however, considered advisable to make a prior test of saline solutions of equal concentration, but not mixed with tannin infusions: 500 c.c. of these solutions evaporated to dryness, then calcined, gave results the averages of which are given in the following table:—

TABLE VI.—SHOWING RELATION OF RESIDUE ON EVAPORATION TO RESIDUE ON IGNITION OF VARIOUS SALTS

	$\text{CaCl}_2\text{aq.}$	$\text{Na}_2\text{SO}_4\text{aq.}$	$\text{Mg}(\text{HCO}_3)_2$
Fixed residue at $105^{\circ}\text{C}$ . . . . .	0.365 gramme	0.260 gramme	0.253 gramme
Ash. . . . .	0.244 „	0.2593 „	0.114 „

Complete drying was finished in a hot-air oven at  $105^{\circ}$  C. ( $221^{\circ}$  F.) until of constant weight, and the ignition was continued for the same length of time occupied in the determination of ash in the analysis of tannin liquors. In order to be able to compare results more easily, the saline matter in solution has been deducted from the weights yielded by the total extract and the total non-tannin. As regards the ash, the result obtained is followed by the result calculated from the preceding data, and from the ash obtained from normal infusions in distilled water, *i.e.* the figures given under the heading "Ash (calculated)" were obtained by adding to the ash given in the preceding Table VI. that of the ash of the tanning material tested. The organic extract was obtained by deducting from the total extract first the figures corresponding to the fixed residue of the preceding table, and then the ash of the total extract obtained by diffusion in distilled water. The ash (obtained as just indicated) was not utilised (1) on account of the differences which exist between the fixed residue and the ash of these saline matters, and (2) because such ash is subject to slight variation, *e.g.* calcium chloride, on prolonged ignition at a high temperature, contains quicklime, and the proportion of quicklime is greater the more rapid the ignition. Losses in weight result, which, according to the percentage and the composition of the tanning material present, may sometimes become sufficiently appreciable as to affect to a certain extent the accuracy of the analytical results. If, again, ignition be not prolonged far enough, as calcium chloride undergoes, when heated, first aqueous and then igneous fusion, it may happen that the carbon is imprisoned in the fused igneous mass and then only burns with great difficulty. Errors of a converse nature to the foregoing may thus occur. If these two errors occur in the same analysis, one in the ash of the total extract and the other in the ash of the non-tannin, the analytical results may thus be very greatly affected. Sodium sulphate may also cause errors. As a general rule, it fuses before the complete combustion of the carbon, and a portion of this cannot be burnt, hence a high result. On the other hand it may, especially when heated rather long at a high temperature, be reduced more or less completely by this carbon, without taking into account that other chemical reactions may occur with the ash of the tanning material present. The following experiments were made on this point: (a) about  $\frac{1}{2}$  litre of sodium sulphate solution containing 0.5 gramme per litre was evaporated, the residue on ignition gave as ash 0.2584 gramme; (b) the ashes were moistened with 50 c.c. of pine infusion. After evaporation and ignition 0.2536 gramme was obtained instead of  $0.2584 + 0.0027 = 0.2611$ ; (c) the last ashes were moistened

in their turn, with 50 c.c. of oak infusion. After evaporation and ignition 0.2572 gramme was obtained instead of 0.2611 gramme + 0.0083 gramme = 0.2694 gramme; (d) this freshly ignited residue was moistened with 50 c.c. of sumac infusion and 0.2778 gramme obtained instead of 0.2694 gramme + 0.0152 gramme = 0.2846. That is to say, the ashes due to the sulphate of soda fall, after the action of pine infusion, to 0.2509 gramme; after the action of oak infusion to 0.2462; after the action of sumac they rise to 0.2516 gramme. It is to be observed that in actual analysis these ashes would be below these figures, because the sodic sulphate operated on would be ten times less. As to bicarbonate of magnesia, it yields oxide by ignition, but the expulsion of the carbonic acid is never complete; moreover, it seems that the bicarbonate is not completely converted into carbonate under the conditions of the determination of the total extract and of the non-tannin, the organic matter present partially hindering its complete decomposition at the temperature of 105° C. (221° F.). Moreover, it will be seen that the actual and the calculated ashes in the tables are seldom represented by the same figures. Endeavours were made to avoid all source of error, because the losses in tannin in the present experiments were not so high as in the researches on the influence of saline matter in the extraction of tannins.

*First Series of Experiments. Action of Salts on Infusion of Tanning Materials. Oak Bark (Table VII).—*The results of the experiments show that salts of lime and magnesia appreciably affected the percentage of total extract as well as that of the organic extract. The turbidity formed was therefore more abundant in infusions charged with such saline matter. All the liquids had, however, precipitated by the end of the third day, but it seems that in the case of the distilled water solutions and the sulphate of soda solutions, the precipitation was due simply to physical causes, whilst in the case of the two other salts it was rather a chemical change which occasioned the loss in extract. The non-tannins, total and organic, behave in quite another way, so that calcium chloride seems not to have affected them, and it follows that the loss in tannin is due solely in this case to precipitation. Sodium sulphate, whilst causing a slight loss in tannin, induced a proportional increase in the non-tannin, so that here the loss in tannin is of a chemical nature, the effect of the salt being to change a portion of the tannin into soluble non-tannin. As to magnesium bicarbonate, it caused a loss in organic extract, which was distributed between the tannin and the non-tannin, the last of the two being especially affected by this saline matter.



TABLE VII.—RESULTS OF EXPERIMENTS ON OAK BARK (PER LITRE OF INFUSION)

	I. Normal Infu- sion.	II. Same containing 0.5 p. 1000 of CaCl <sub>2</sub> .	III. Same containing 0.5 p. 1000 of Na <sub>2</sub> SO <sub>4</sub> .	IV. Same containing 0.5 p. 1000 of Mg(HCO <sub>3</sub> ) <sub>2</sub> .
Extract total <sup>1</sup> . . .	4.988	4.760 - 0.228	4.950 - 0.038	4.834 - 0.154
„ ash <sup>2</sup> . . .	0.166	0.582 + 0.416	0.706 + 0.540	0.386 + 0.220
„ „ <sup>3</sup> . . .	0.166	0.654 + 0.488	0.686 + 0.520	0.394 + 0.228
„ actual organic . . .	4.822	4.594 - 0.228	4.784 - 0.038	4.668 - 0.152
Non-tannin total <sup>1</sup> . . .	1.630	1.618 - 0.012	1.750 + 0.120	1.528 - 0.102
„ ash <sup>2</sup> . . .	0.126	0.656 + 0.530	0.678 + 0.552	0.324 + 0.158
„ „ <sup>3</sup> . . .	0.126	0.614 + 0.488	0.646 + 0.520	0.354 + 0.228
„ actual organic . . .	1.504	1.492 - 0.012	1.624 + 0.120	1.402 - 0.102
Fixed by hide, total . . .	3.358	3.142 - 0.216	3.200 - 0.158	3.206 - 0.052
Tannin . . .	3.318	3.102 - 0.216	3.160 - 0.158	3.266 - 0.052
„ lost per cent. . .	0.0	6.51	4.79	1.56

TABLE VIII.—RESULTS OF EXPERIMENTS ON PINE BARK (PER LITRE OF INFUSION)

	I. Normal Infu- sion.	II. Same containing 0.5 p. 1000 of CaCl <sub>2</sub> .	III. Same containing 0.5 p. 1000 of Na <sub>2</sub> SO <sub>4</sub> .	IV. Same containing 0.5 p. 1000 of Mg(HCO <sub>3</sub> ) <sub>2</sub> .
Extract total <sup>1</sup> . . .	4.212	3.936 - 0.276	4.234 + 0.022	3.970 - 0.242
„ ash <sup>2</sup> . . .	0.054	0.372 + 0.318	0.522 + 0.468	0.370 + 0.316
„ „ <sup>3</sup> . . .	0.054	0.542 + 0.488	0.574 + 0.520	0.282 + 0.228
„ actual organic . . .	4.158	3.882 - 0.276	4.180 + 0.022	3.916 - 0.242
Non-tannin total <sup>1</sup> . . .	0.790	0.916 + 0.126	0.940 + 0.150	0.958 + 0.168
„ ash <sup>2</sup> . . .	0.038	0.648 + 0.610	0.586 + 0.548	0.232 + 0.194
„ „ <sup>3</sup> . . .	0.038	0.526 + 0.488	0.558 + 0.520	0.266 + 0.228
„ actual organic . . .	0.752	0.878 + 0.126	0.902 + 0.150	0.904 + 0.52
Fixed by hide . . .	3.422	3.020 - 0.402	3.294 - 0.128	3.012 - 0.410
Tannin . . .	3.406	3.004 - 0.402	3.278 - 0.128	3.012 - 0.394
„ lost per cent. . .	0.0	11.80	3.90	11.56

*Action on Pine Bark* (Table VIII).—As in the case of oak, the total extract and the organic extract were lowered in the infusions to which calcium chloride and magnesium bicarbonate were added. These salts caused very appreciable loss in tannin. In both cases, besides precipitation of tanning matter, there was partial conversion of tannin into soluble non-tannin, as the increase of organic non-tannin in Columns II. and IV. shows. There was therefore partial dissociation of the tanning matter or reaction of the tannin with the saline matter, with production of compounds, non-assimilable by the skin, in the conditions of analysis. Oak tannin behaves in no way the same, because the non-tannins in Columns II. and IV. are, especially in IV., in a decreasing ratio. Oak tannin appears, therefore, less sensitive

<sup>1</sup> Saline matter deducted.<sup>2</sup> Saline matter included.<sup>3</sup> Calculated.

TABLE IX.—RESULTS OF EXPERIMENTS ON SUMAC (PER LITRE OF INFUSION)

	I. Normal Infu- sion.	II. Same containing 0.5 p. 1000 of CaCl <sub>2</sub> .		III. Same containing 0.5 p. 1000 of Na <sub>2</sub> SO <sub>4</sub> .		IV. Same containing 0.5 p. 1000 of Mg(HCO <sub>3</sub> ) <sub>2</sub> .	
Extract total <sup>1</sup> . . .	5.868	5.888	+0.020	5.996	+0.128	5.878	+0.010
„ ash <sup>2</sup> . . .	0.304	0.566	+0.262	0.862	+0.558	0.582	+0.278
„ „ <sup>3</sup> . . .	0.304	0.792	+0.488	0.824	+0.520	0.532	+0.228
„ actual organic . . .	5.564	5.584	+0.020	5.692	+0.128	5.574	+0.010
Non-tannin total <sup>1</sup> . . .	2.654	2.610	-0.044	2.836	+0.182	2.762	+0.108
„ ash <sup>2</sup> . . .	0.354	0.744	+0.390	0.886	+0.532	0.508	+0.154
„ „ <sup>3</sup> . . .	0.354	0.842	+0.488	0.874	+0.520	0.582	+0.228
„ actual organic . . .	2.300	2.256	-0.044	2.482	+0.182	2.408	+0.108
Fixed by hide . . .	3.214	3.278	+0.064	3.160	-0.054	3.116	-0.098
Tannin . . .	3.264	3.308	+0.044	3.210	-0.054	3.166	-0.098
„ lost per cent. . .	0.00	0.00		1.65		3.00	

to these changes than pine tannin. Sodium sulphate behaves similarly as with oak bark, a slight increase in non-tannin with a proportional decrease in tannin. The turbidity formed in the saline infusion was less than that formed in the distilled water infusion, because the organic extract and total extract are slightly increased. Here again the chemical rôle of sodium sulphate in the transformation of tannin into non-tannin is confirmed.

*Action on Sumac* (Table IX.).—The precipitation was about the same in the four tests. But in the sodium sulphate infusion it was less pronounced than in the other liquids, even than in the distilled water infusion; it follows that the total extract and organic extract only differ slightly. Calcium chloride seems to have no effect on sumac solutions. Sodium sulphate produced a comparatively small loss in tannin, but caused a three-fold greater increase in non-tannin, from which one would be inclined to conclude that the slight solvent action of sodium sulphate on the precipitate formed by distilled water acts more on the non-tannin than on the tannin; this also occurs with pine extract, though to a less extent (Table VIII.). The action of magnesium bicarbonate is more apparent, the saline matter, without inducing increased turbidity, giving a precipitate of tanning matter or of one or other of its constituents, hence a loss of tannin equivalent to the increase in organic non-tannin. It therefore appears to behave with sumac in a purely chemical fashion in changing tannin into soluble non-tannin.

*Conclusion I.*—It follows from these preceding experiments that saline matters may behave differently towards tanning infusions; they either (a) only act slightly, *e.g.* towards sumac,

<sup>1</sup> Saline matter deducted.<sup>2</sup> Saline matter included.<sup>3</sup> Calculated.

or (b) they induce a loss in tannin without increasing the turbidity, which always occurs, even when distilled water has been used in extraction, *e.g.* action of sulphate of soda on oak and pine infusions. This action of sulphate of soda is difficult to explain with any degree of certainty. The loss found may be due to a partial change of tannin into a substance unassimilable by the skin, as well as to combination of the tanning matter with the saline matter, to form a compound which would not be retained by the skin. It may even be said that sodium sulphate alters the osmotic properties of the skin, so that it becomes no longer capable of retaining the whole of the tannin. But contrary to this point of view, in no case was any trace of tannin to be found in the liquid passing through Procter's filter. Again, as will be seen later, sodium sulphate behaves in quite a different way with concentrated solutions of quebracho extract, in which it induces no loss in tannin. (c) They induce a loss in tannin whilst increasing the precipitate formed. This occurs with magnesium and calcium salts, but these can, in certain cases, behave like sodium sulphate, by changing partially the tannin into soluble non-tannin. The turbidity is not always due to a precipitate of tannin, but in certain cases non-tannin is also carried down. It may be said generally that the saline matters, dissolved in natural waters, still further accentuate after extraction the loss already incurred during extraction, whether they precipitate tannin or induce its conversion into substances unassimilable by hide powder. By the prolonged contact of saline matters with tannin infusions, it may be taken that the losses in tannin become still more appreciable, judging from the precipitates which afterwards occurred in the clear liquors used for analysis. The following are the observations made on these liquors a fortnight after the foregoing tests: (1) The oak solutions were quite turbid except No. 2 (calcium chloride), which showed traces of mould growth. (2) The pine solutions remained limpid except No. 2. (3) The sumac solutions likewise remained limpid except No. 4, which presented an abundant deposit. All the infusions containing magnesium bicarbonate were very dark, even sumac infusion.

*Conclusion II.*—Before drawing the second conclusion which results from our experiments, the losses in tannin which occurred in these latter experiments have to be compared with those found previously during the examination of the action of saline matter on the extraction of tannins. The losses in tannin corresponding to solutions of 0.5 gramme per litre of calcium chloride, sodium sulphate, and magnesium bicarbonate were calculated by interpolation from the tabulated results of this latter research, but the results of the present experiments have been brought to 100 parts of the tanning substance used. We

thus got the following table, in which are given in horizontal lines corresponding to the letter A, the percentages of tannin when the saline matter is added to the infusion previously prepared in distilled water, and, in the horizontal lines corresponding to the letter B, the percentages obtained when the extraction is made with the saline solution.

TABLE X.—SHOWING DIFFERENT RESULTS OBTAINED (A) BY EXTRACTING TANNIN BY DISTILLED WATER AND THEN ADDING SALINE SOLUTIONS, AND (B) BY USING THE SALINE SOLUTION FOR EXTRACTION

		I Distilled Water Infusion.	II. Same with 0.5 p. 1000 of CaCl.		III. Same with 0.5 p. 1000 of Na <sub>2</sub> SO <sub>4</sub> .		IV. Same with 0.5 p. 1000 of Mg(HCO <sub>3</sub> ) <sub>2</sub> .	
Oak tannin	{ A .	12.02	11.24	- 0.78	11.56	- 0.46	11.73	- 0.29
	{ B .	...	9.04	- 2.98	10.48	- 1.54	8.15	- 3.87
Pine tannin	{ A .	19.13	17.59	- 1.54	18.63	- 0.50	17.00	- 2.13
	{ B .	...	15.10	- 4.03	15.72	- 3.41	16.04	- 3.09
Sumac tannin	{ A .	18.66	18.69	+ 0.03	18.35	- 0.31	18.10	- 0.56
	{ B .	...	16.40	- 2.26	17.12	- 1.54	15.54	- 3.12

The differences between the figures given in the lines A and B are considerable; the losses in tannin observed in the preceding experiments were much lower than those obtained in the experiments relating to the action of salts on extraction. That may be due to two causes: (1) The fact that the absence of vegetable cells containing tanning matters did not induce osmotic phenomena, and consequently the electro-chemical actions to which the previous losses in tannin were attributed. (2) The fact that heat was used during the extraction of the tannins, and that consequently the saline matters were able to act in the hot state more energetically than at the ordinary temperature. It is quite certain that heat influences the results which vary according to whether the operation is done in the cold or in the hot state. This was well demonstrated in the first examination on the action of Belgian tannery waters in the extraction, but it is especially in the osmotic phenomena that the effect of heat is most felt. It is to facilitate this osmosis that the diffusers are heated as much in the sugar industry as in the manufacture of tannin extracts. In the absence of vegetable cells it ought to exert a secondary influence, judging from the results given in the following paragraph, in regard to quebracho extract. That extract was dissolved in the hot state, and consequently the saline matters reacted at a comparatively high temperature. Now the losses in tannin are of the same class as in the preceding experiments. Even sodium sulphate has no more action than in the experiments of Table IX. relating to sumac. There

is, therefore, in this comparison of results a confirmation of the explanation given above of the losses in tannin, losses which were attributed to phenomena of an electro-chemical nature. A practical conclusion to draw from this is, that in using a water charged with mineral matters for the extraction of tannin every advantage is to be gained by working on tannin materials ground as finely as possible, if it be desired to prevent the destruction of tannin; remembering, however, that the finer the grinding the greater is the number of torn cells, and consequently the more is the quotient of purity of the liquor diminished. The influence of this fact is not yet appreciated in tanneries.

*Second Series of Experiments. Action of Saline Matter on Tannin Extracts.*—A large quantity of tannin extracts being now used in tanning, it is interesting to ascertain the action of saline water on the solution of these extracts. The two products most commonly used were submitted to the previous tests, the quebracho extract and chestnut extract. Mimosa extract D, made by Le Petit Dollfus and Ganssner of Milan, was also tested. It is known that this highly decolorised extract is completely soluble in cold water, and yields quite superior results in tanning. The action of saline matter on this extract is of interest on account of the comparatively high amount of ash which it left on ignition, which is greater even than that of the mineral matter used in the tests.

*Quebracho Extract.*—The quebracho extract was submitted to three experiments: (1) In the first the amount of material taken was such as to have a concentration double that of the normal concentration prescribed for analysis. The product was dissolved in boiling distilled water, then, after the amount taken for analysis was run into the graduated flask, boiling water was added up to three-fourths of its volume, and allowed to cool down after adding the saline matter in sufficient water to yield to the total liquid a concentration of 0.05 per cent. (0.5 grammes per litre). Each liquid was analysed on the third day, after being stored without dilution with an equal volume of water, *i.e.*, under conditions outside the conditions imposed by the International Association of Leather Trades Chemists. The results obtained are given in Table XI. They show a loss in tannin of 1.6 per cent. as regards the liquor charged with calcium chloride and of 1.8 per cent. as regards the water charged with sodium bicarbonate. It was observed that the liquid which had passed through the Procter's filter in the first case (Column II) contained small amounts of tannin, which means that the loss of 1.6 per cent. is exaggerated. Moreover, very peculiarly, instead of finding that sodium sulphate, instead of inducing a loss in tannin, on the contrary gave an increase of assimilable matter.

These two facts rendered it necessary to make a second series of experiments. (2) This second series was conducted in a slightly different manner. The same quantity of material was weighed and dissolved in, or at least beaten up with, the least possible amount of tepid water, run into the graduated flask, cold water added, and finally the saline matter to be dissolved. The operation in this case was practically carried out in the cold, whilst in the first case it was done in the hot state. Besides, the filtered liquors after three days were diluted with an equal volume of distilled water before being passed through the hide powder. The results of the analysis are given in Table II. The loss produced by magnesium salts was about the same, whilst, as anticipated, the loss due to calcium salts had increased. But the liquid clarified by filtration precipitated at the end of some days. As regards sulphate of soda, it behaved absolutely the same way as in the first instance. In the two experiments the substances retained by the hide powder being increased by 0.6 per cent. This fact, coinciding with a notable diminution in the ash of the non-tannin as compared with the rest of the total extract seems to indicate that a portion of the fine matter was absorbed by the hide powder, but as this does not reoccur in Table XII., which gives the results of analysis made on a solution of quebracho extract of normal concentration, it is reasonable to suppose that in the former case a kind of combination takes place between the saline matters and the tannin of quebracho, forming a substance capable of being absorbed by the hide and which would be produced in presence of an excess of tannin. The high percentages of ash found in leathers tanned with quebracho are perhaps due to similar causes. It appears from a comparison of the two tables that the application of heat to dissolve the extract is prejudicial to the solution of the tannin, the percentage of which approaches, in the second case, that obtained in the normal solution (see Table XIII.). The prolonged action of heat, instead of bringing more matter into solution, induces, on the contrary, in pure water and in water charged with sodium sulphate, precipitations which diminish the total extract and the organic extract. But the converse occurs with water charged with salts of the alkaline earths. Another and more important fact, which is brought out by these experiments, is the increased amount of the non-tannin dissolved by the action of heat. But if solution be effected in the cold, a portion of the non-tannin is precipitated by salts of the alkaline earths. This fact is of importance in relation to the viscosity of the liquor. (3) The third series of experiments (Table III.) was conducted under normal conditions as regards concentration of the solutions. The decrease of total extract and organic extract is in the same ratio as in the preceding series,

*i.e.* the precipitation was less in solutions containing sodium sulphate and greater in solutions charged with calcium chloride. The percentage of tannin found in the case of a solution of normal concentration approaches that given in the preceding table. In fact, sodium sulphate causes no increase in matter assimilable by the skin; but, on the contrary, results in a slight loss, of the same nature as that found with infusions of tanning materials.

*Chestnut Extract* (Table XIV.) is especially sensitive to magnesium bicarbonate, which appears to act physically, since it produces no appreciable increase of organic non-tannin. The other saline matters, on the contrary, act chemically, especially sodium sulphate. These salts, however, also act by precipitation, as shown by the decrease in organic extract. The action of sodium sulphate is quite peculiar, for the like does not occur with any other extract. Moreover, the method of manufacture must in many instances influence these changes in composition. The loss caused by magnesium bicarbonate, already considerable, would increase with time, because the liquid, after clarification by filtration, showed an abundant deposit in a fortnight. The ash of the non-tannin is half that of the total extract. It would, therefore, seem that in this case a portion of the compound which the tannin forms with the salt was absorbed by the hide powder, leading to a greater actual loss of tannin than is shown by the figures.

*Mimosa D.* (Table XV.) is entirely soluble in cold water. It gives no precipitate, either with sodium sulphate or with magnesium bicarbonate. Calcium chloride alone causes turbidity. Independently of this physical action, all the three saline substances always reacted chemically. Sodium sulphate produced only a slight loss in tannin, with a proportional increase in non-tannin. It appears to have a similar action upon all the substances examined, chestnut extract excepted. This is interesting, because if that is the case the ordinary purification of selenitic water may yield good results as far as the solution of tannic extracts is concerned. Magnesium salts, or at least the bicarbonate, have also little effect, but it is not the same with calcium salts, which affect mimosa like chestnut extract by reacting physically and chemically. After a fortnight the three clear solutions of mimosa extract were still perfectly limpid. A curious thing is that the mineral matter contained in this clear extract seems to have no effect on its composition, whether such mineral matter consists of inert salts, sodium sulphate, for example, or whether it exists as organic compounds. In the latter case they are not retained by hide powder, as is shown by the ash of the non-tannin.

Summing up, it may be said that in these experiments the

tannin materials examined behave towards saline matter like infusions of tanning substances. The losses are small compared with those produced in the extraction of the latter. Moreover, a little less regularity is noticeable with tannin extracts, but it is possible that the method of manufacture must be taken into account.

TABLE XI.—RESULTS OF FIRST EXPERIMENTS ON QUEBRACHO EXTRACT. DOUBLE NORMAL INFUSION—EXPRESSED AS PER CENTS. BY WEIGHT OF EXTRACT TESTED

	I. Double Normal Infu- sion.	II. Same with 0.5 p. 1000 of CaCl <sub>2</sub> .	III. Same with 0.5 p. 1000 of Na <sub>2</sub> SO <sub>4</sub> .	IV. Same with 0.5 p. 1000 of Mg(HCO <sub>3</sub> ) <sub>2</sub> .			
Extract total <sup>1</sup> . . .	42.250	41.120	- 1.130	42.350	+ 0.100	41.530	- 0.720
„ ash <sup>2</sup> . . .	1.325	2.850	+ 1.525	3.875	+ 2.550	2.580	+ 1.255
„ „ <sup>3</sup> . . .	1.325	3.765	+ 2.440	3.025	+ 2.600	2.465	+ 1.140
„ actual organic . . .	40.925	39.800	- 2.125	41.025	+ 0.100	40.205	- 0.720
Non-tannin total <sup>1</sup> . . .	5.100	7.200	+ 2.100	4.575	- 0.525	6.190	+ 1.090
„ ash <sup>2</sup> . . .	1.425	2.100	+ 0.675	2.225	+ 0.800	3.875	+ 2.450
„ „ <sup>3</sup> . . .	1.425	3.865	+ 2.440	4.025	+ 2.600	2.565	+ 1.140
„ actual organic . . .	3.675	5.775	+ 2.100	3.150	- 0.525	4.770	+ 1.095
Fixed by hide . . .	37.150	33.920	- 3.230	37.775	+ 0.625	35.340	- 1.810
Tannin . . .	37.250	34.025	- 3.225	37.875	+ 0.625	35.435	- 1.815
„ loss per cent.	0.0	8.6		0.0		4.86	

TABLE XII.—RESULTS OF FIRST EXPERIMENTS ON QUEBRACHO EXTRACT. DOUBLE NORMAL SOLUTIONS—EXPRESSED IN PER CENTS. BY WEIGHT OF EXTRACT TESTED

	I. Double Normal Infusion.	II. Same with 0.5 p. 1000 of CaCl <sub>2</sub> .	III. Same with 0.5 p. 1000 of Na <sub>2</sub> SO <sub>4</sub> .	IV. Same with 0.5 p. 1000 of Mg(HCO <sub>3</sub> ) <sub>2</sub> .			
Extract total <sup>1</sup> . . .	44.77	38.30	- 6.47	43.50	- 1.20	40.29	- 3.48
„ ash <sup>2</sup> . . .	1.25	...	...	...	...	...	...
„ „ <sup>3</sup> . . .	1.25	...	...	...	...	...	...
„ actual organic . . .	43.52	37.05	- 6.47	42.25	- 1.20	39.04	- 3.48
Non-tannin total <sup>1</sup> . . .	5.2	1.40	- 3.80	3.35	- 1.85	2.49	- 2.71
„ ash <sup>2</sup> . . .	1.05	...	...	...	...	...	...
„ „ <sup>3</sup> . . .	1.05	...	...	...	...	...	...
„ actual organic . . .	4.15	0.35	- 3.80	2.30	- 1.85	1.44	- 2.71
Total fixed by hide . . .	39.57	36.90	- 2.67	40.15	+ 0.58	37.80	- 1.77
Tannin . . .	39.37	36.70	- 2.67	39.95	+ 0.58	37.60	- 1.77
„ loss per cent. . .	0.0	6.78		0.0		4.50	

<sup>1</sup> Saline matter deducted.

<sup>2</sup> Saline matter included.

<sup>3</sup> Calculated.



TABLE XIII.—RESULTS OF SECOND EXPERIMENTS ON QUEBRACHO EXTRACT. NORMAL  
—EXPRESSED IN PARTS BY WEIGHT PER CENT. OF EXTRACT TESTED

	I. Normal Infu- sion.	II. Same with 0.5 p. 1000 of $\text{CaCl}_2$ .	III. Same with 0.5 p. 1000 of $\text{Na}_2\text{SO}_4$ .	IV. Same with 0.5 p. 1000 of $\text{Mg}(\text{HCO}_3)_2$ .
Extract total <sup>1</sup> . . . .	45.04	42.50 - 2.54	43.90 - 1.14	43.19 - 1.85
„ ash <sup>2</sup> . . . .	2.30	3.50 + 1.20	6.25 + 3.95	4.20 + 1.90
„ „ <sup>3</sup> . . . .	2.30	7.18 + 4.88	7.50 + 5.20	4.58 + 2.28
„ actual organic . . . .	42.74	40.20 - 2.54	41.60 - 1.14	40.89 - 1.85
Non-tannin total <sup>1</sup> . . . .	5.85	4.85 - 1.00	5.45 - 0.40	6.19 + 0.34
„ ash <sup>2</sup> . . . .	1.90	6.75 + 4.85	6.55 + 4.65	4.05 + 2.15
„ „ <sup>3</sup> . . . .	1.90	6.78 + 4.88	7.10 + 5.20	4.18 + 2.28
„ actual organic . . . .	3.95	2.95 - 1.00	3.55 - 0.40	4.79 + 0.34
Total fixed by hide . . . .	39.19	37.65 - 1.54	38.45 - 0.74	37.00 - 2.19
Tannin . . . .	38.79	37.25 - 1.54	38.05 - 0.74	36.60 - 2.19
„ loss per cent. . . .	0.0	3.97	1.91	5.64

TABLE XIV.—RESULTS OF EXPERIMENTS ON CHESTNUT EXTRACT—EXPRESSED AS PER  
CENTS. BY WEIGHT OF EXTRACT TESTED

	I. Normal Infu- sion.	II. Same with 0.5 p. 1000 of $\text{CaCl}_2$ .	III. Same with 0.5 p. 1000 of $\text{Na}_2\text{SO}_4$ .	IV. Same with 0.5 p. 1000 of $\text{Mg}(\text{HCO}_3)_2$ .
Extract total <sup>1</sup> . . . .	37.332	35.441 - 1.891	35.989 - 1.343	34.667 - 2.665
„ ash <sup>2</sup> . . . .	0.803	2.810 + 2.007	3.723 + 2.920	2.445 + 1.612
„ „ <sup>3</sup> . . . .	0.803	5.683 + 4.880	6.003 + 5.200	3.083 + 2.28
„ actual organic . . . .	36.529	34.638 - 1.891	35.186 - 1.343	33.864 - 2.665
Non-tannin total <sup>1</sup> . . . .	9.855	10.402 + 0.547	10.801 + 0.949	10.030 + 0.175
„ ash <sup>2</sup> . . . .	0.839	4.088 + 3.249	3.942 + 2.103	1.004 + 0.255
„ „ <sup>3</sup> . . . .	0.839	5.719 + 4.880	6.039 + 5.200	3.119 + 2.280
„ actual or- ganic . . . .	9.016	9.5635 + 0.547	9.965 + 0.949	9.121 + 0.175
Total fixed by hide . . . .	27.477	25.039 - 2.438	25.185 - 2.292	24.637 - 2.840
Tannin . . . .	27.513	25.071 - 2.439	25.221 - 2.292	24.672 - 2.841
„ loss per cent. . . .	0.00	8.86	8.31	10.31

TABLE XV.—EXPERIMENTS ON MIMOSA EXTRACT D—EXPRESSED IN PER CENTS. BY  
WEIGHT OF EXTRACT TESTED

	I. Normal Infu- sion.	II. Same with 0.5 p. 1000 of $\text{CaCl}_2$ .	III. Same with 0.5 p. 1000 of $\text{Na}_2\text{SO}_4$ .	IV. Same with 0.5 p. 1000 of $\text{Mg}(\text{HCO}_3)_2$ .
Extract total <sup>1</sup> . . . .	48.41	45.70 - 1.74	48.50 + 0.06	48.39 - 0.05
„ ash <sup>2</sup> . . . .	6.41	9.60 + 3.16	12.10 + 5.66	9.30 + 2.86
„ „ <sup>3</sup> . . . .	6.41	11.32 + 4.88	11.64 + 5.20	8.72 + 2.28
„ actual organic . . . .	42.00	40.26 - 1.74	42.06 + 0.06	41.95 - 0.05
Non-tannin total . . . .	10.55	12.50 + 1.95	11.40 + 0.85	12.19 + 1.64
„ ash <sup>2</sup> . . . .	6.30	11.40 + 5.10	12.15 + 5.85	8.85 + 2.55
„ „ <sup>3</sup> . . . .	6.30	11.18 + 4.88	11.50 + 5.20	8.58 + 2.28
„ actual organic . . . .	4.25	6.20 + 1.95	5.10 + 0.85	5.89 + 1.64
Total fixed by hide . . . .	37.89	34.20 - 3.69	37.10 - 0.79	36.20 - 1.69
Tannin . . . .	37.75	34.06 - 3.69	36.96 - 0.79	36.06 - 1.69
„ loss per cent. . . .	0.0	9.74	2.08	4.46

<sup>1</sup> Saline matter deducted.

<sup>2</sup> Saline matter included.

<sup>3</sup> Calculated.

*Various Chestnut Liquors and Extracts. Analytical Tables showing Compositions.*—Commercially, it requires on an average 1300 to 1400 kilogrammes of liquor of the following composition A which generally indicates 3·8° to 4·5° B., to produce 100 kilogrammes of chestnut extract of 25° B., or a yield of 7 to 8 per cent. :—

TABLE XVI.—SHOWING COMPOSITION OF VARIOUS CHESTNUT WOOD LIQUORS AND EXTRACTS

	A.	B.	C.	D.	E.	F.	G.	H.
Soluble tanning substances .	3·92	29·20	29·25	28·38	34·30	36·00	19·60	43·00
Non-tannins .	2·36	10·0	13·16	10·69	15·80	14·00	12·20	37·70
Water .	93·47	60·60	57·42	60·11	48·90	48·70	66·30	19·00
Insoluble .	0·25	0·20	0·17 <sup>1</sup>	0·82 <sup>1</sup>	1·00	1·30	1·90	0·30
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

A, chestnut liquor, total soluble, 6·28.—B, chestnut extract 25°, rational manufacture, from a factory treating a mixture of Lyonnais, Charollais, and Dauphiné wood. Density at 18° C. = 1·207 (25·2° B.). A well-clarified extract, fairly well decolorised, scarcely becoming turbid when cold, even after long standing of the solution.—C, 25° chestnut extract made at the factory at Génolhac, Gard, by Ausset and Hermet. Very fluid, decolorised, very readily soluble in the cold.—D, 25° chestnut extract from the factory of Roubin et Cie at Lalevade, Ardèche. Extract well clarified and decolorised, very soluble in the cold, made exclusively with Ardèche wood.—E, 30° chestnut extract of La Société des produits Chimiques de Saint Chamond, Loire. Fairly well decolorised, gives a slight turbidity with cold water and deposits rapidly on standing. This factory employs a mixture of Lyonnais, Auvergne, and Vivarais wood.—F, analysis of 30° chestnut extract from a Corsican factory. Clarified, but only slightly decolorised, with a somewhat thick deposit on standing.—G, 20° chestnut extract ("Gallique") for dyeing, made as mentioned from unbarked wood and the concentration of the crude liquors from the maceration (under a pressure of 2 kilogrammes). This extract becomes cloudy in cold water, and even in hot water yields a dark brown solution which is, however, of no importance, as this product is intended for dyeing or for the manufacture of boiler fluid.—H, dry chestnut extract made by concentrating 25° extract at 45° in a rotary apparatus *in vacuo*. Very soluble in water, when it gives only a slight turbidity.

On the extraction of tanning materials, and the amount of residual or ineffective tannin in the leached materials, see W. Fitner, *Gerber*, 1908, pp. 291, 305, 319, 333.

*Loss of Tannin in Weak Tannin Liquors.*—J. Paessler<sup>2</sup> has made numerous experiments on weak tannin solutions (2 to 3 per cent.) from various materials to determine the losses of tannin which occur on keeping and divides them into three classes (1) Liquors which show practically no diminution of tannin

<sup>1</sup> Ash.

<sup>2</sup> *Collegium*, 1904, pp. 277, 284, 293.

(0 to 4 per cent.) after standing sixty days, including mangrove, mimosa, sumach, quebracho, and gambier. (2) Liquors which suffer a moderate diminution (7.5 to 16 per cent.) including oak bark, oak wood extract, pine bark, and knopperrn. (3) Liquors which lose very considerable amounts of tannin (23 to 29 per cent.) including trillo, myrabolams, valonia, and divi-divi.

## CHAPTER II

### PLANT AND EQUIPMENT FOR TREATING CHESTNUT WOOD

*System of Heating—Steam Boilers—Management and Upkeep  
—Furnaces and Various Gas Producers—Chimneys—  
Steam Engines—Cutters—Cup Elevators—Conveyers*

*Boilers with Two "Bouilleurs" with or without Reheaters.—*  
The system, with great reserves of water and steam, with economical results, allowing the fixing of grates of large section for the adaptation of generator furnaces burning the waste or chips of the exhausted wood is that to be recommended for extract factories. Fig. 75 shows a boiler of this kind.

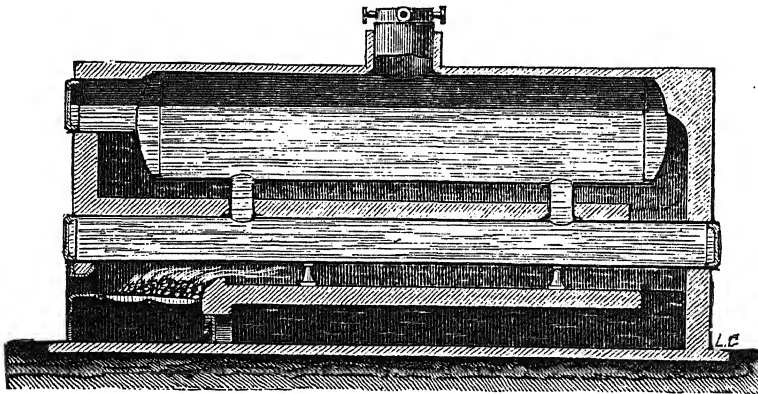


FIG. 75.—Boilers with two bouilleurs.

*"Multibouilleur" Boilers with Reheaters.—*System, with great reserves of water and steam, allowing the use of very variable quantities of steam without inconvenience. Methodical heating, easy cleaning. Very good calorific results. Recommended for large tanneries and extract factories, permitting also the special adaptation of gas generator furnaces burning spent tan or exhausted wood chips with 55 or 60 per cent. of moisture. Fig. 76 shows a boiler of this kind; the tops of the heads of the bouilleurs and the reheaters are made of stamped steel. In a

general way, in normal working the boiler vaporises about 14 kilogrammes per square metre of heating surface.

*Boilers with Interior Furnaces and Galloway Tubes.*—Finally, a type of this kind is shown in Fig. 77. It is that which is most suitable for an extract factory and in which the calorific utilisation of the hot gases is a maximum, with an enormous evaporating capacity.

*Management of the Boilers.*—In the case of three boilers, Nos. 1, 2, 3, one of which is standing.

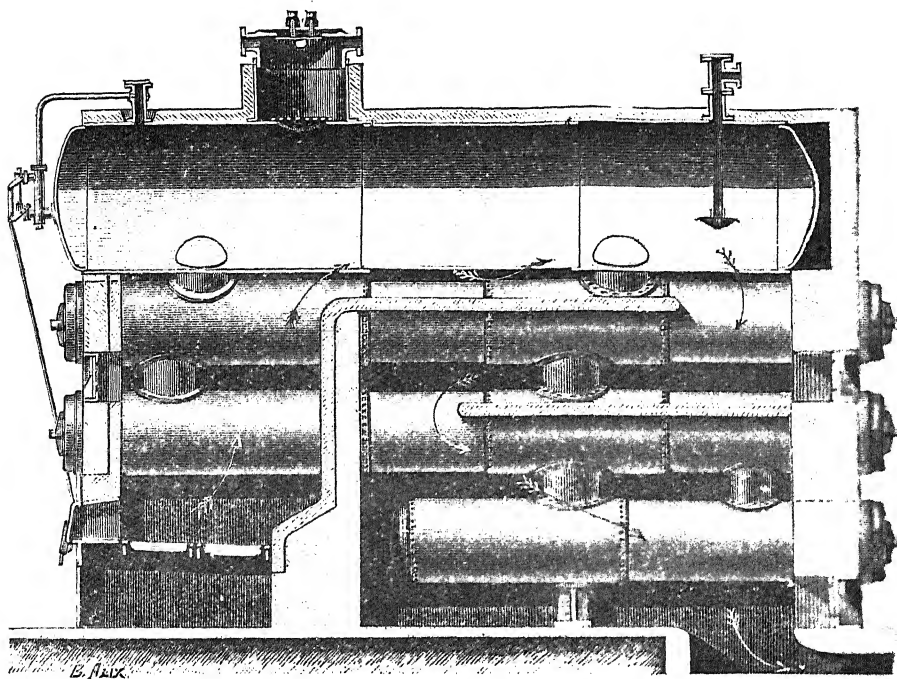


FIG. 76.—Multitubulaire boiler.

*Rotation of Boilers and Cleaning.*—The boilers are worked on the rotation system so that each boiler is changed every two months, in such a way that each works during four consecutive months. Each time that the boiler is changed, that is to say, every two months in normal working, it is necessary, as soon as the boiler is cold, to empty it, remove the manhole, inspect the interior, scrape off any encrustation, clean the smoke flues, close up the manhole, fill it up again so as to bring it in a state fit for working as soon as possible, to be ready if any accident should happen to the other boilers.

*Extractions.*—If the water be strongly calcareous (very hard) it will be necessary to blow off every morning from each boiler so as to remove the mud in the boilers. Each blow off should amount to about 20 cm. (8 inches) of water. To blow off from a boiler all that needs to be done is to open the tap of one of the lower *bouilleurs* and allow the level to fall 10 cm. (4 inches), close that tap and open the tap of the other to lower its level 10 cm. (4 inches), and close that tap.

*Water-Level.*—The water-level ought always to be kept as near as possible to the line marked on the gauge glass. It should not be allowed to fall nor rise more than 10 cm. (4 inches) above or below the normal level. If, by accident, the level falls lower, and especially if no water is to be seen in the gauge glass, the boiler is in danger of explosion. In that case it is necessary to feed the boiler immediately and to close the damper com-

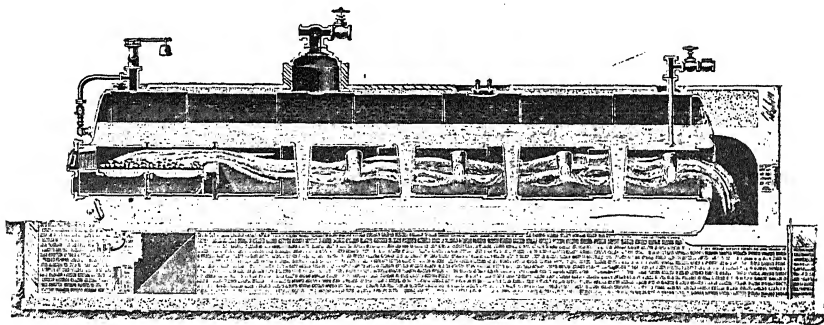


FIG. 77.—Boiler with two interior cylindrical furnaces with Galloway tubes in the furnaces.

pletely, so as to cut off the supply of heat. If the water-level rises higher than 10 cm. (4 inches) above the normal level, there is a risk of water being carried over by the steam, thus causing the engine cylinders to jump. In that case the water feed must be immediately shut off, and sufficient water run off to bring the water to its normal level. These are two of the gravest faults on the part of an engine-driver. They may cause an explosion in the boiler or the steam engines. Each morning the engine-driver ought to manipulate all the water-level (gauge glass) taps, not only those on the cast-iron foundation, but those used for blowing off. This precaution is necessary to see that the taps do not become fast and incapable therefore of being turned instantly at the moment when a gauge glass breaks.

*Pressure.*—The driver is entrusted with the manipulation of the registers (dampers) so as to increase or arrest the draught according to the indications of the pressure gauge. Each

morning he should mount the boilers, and lift gently but very slightly by hand each of the safety valves, so as to cause them to blow off. This precaution cleans the seat of the valves, and prevents any adherence which might occur should they seldom or never blow off. When the pressure rises above what is required, and the valves blow off strongly, the principal dampers must be closed, the boilers fed a little more rapidly (unless the water-level be not already too high), and arrangements made with the man in charge of the autoclaves or steam engines to use a little more steam, if possible, for a time, until the pressure is reduced to its normal figure. The engine-driver ought to repair forthwith any leakage which may occur in the valves of all the boiler mountings.

*Feed Pumps and Boiler Valves.*—The valve for steam, which supplies the feed pumps, ought to be entirely open.

*Starting the Pumps.*—To start a pump, first open the two blow-off cocks of the steam cylinder (these should really be left open since the preceding stoppage), then open very slightly the steam valve on the pump to blow off the condensed water contained in the pipe and cylinder. When no more water issues from the blow-off taps close them, and open out the steam valve until the speed of the pump is attained.

*Speed of the Pump.*—One pump alone must be kept constantly at work at reduced speed without ever stopping. This method of working greatly preserves the pumps, and results in more steam being generated from the boilers. If, in order to keep the boilers supplied with water, it is necessary to work a pump at rather high speed, but which never ought to reach more than 80 to 90 strokes, this is a sign that the water piston has too much play in its cylinder; it must then be dismantled and its packing renewed.<sup>1</sup>

*Stopping the Pump.*—To stop the pump the steam valve must be completely closed and the blow-off cocks of the steam cylinder opened.

*Pump Joints.*—(1) The joints of the bottoms of the cylinders and of the bell for the return air ought to be made from a sheet of thick paper or of thin, carefully cut rubber. (2) The water piston ought to be packed with tallowed hemp for cold water, bronze for hot water. (3) The packing of the stuffing boxes with glands, piston rods, ought to be made with a layer of fine asbestos. Such stuffing boxes ought to be screwed up as lightly as possible, just sufficiently to prevent escape of steam.

*Inspecting the Plunger.*—If the pump does not work properly, it is generally due to the plunger. This must then be inspected, but for this purpose it is not necessary to remove the plunger

<sup>1</sup>To obviate intermittent feeding Koerting's automatic feeder is now used. It constantly normal working is a real safeguard.—J. N.

box; it may be necessary to clean it as well as its seat, but it must never be filed. The plunger ought to be replaced in the direction in which it was taken out.

*Lubricator.*—The lubricator ought always to be open, and the jet which regulates the supply of oil ought always to be adjusted to the same mark so that the flow is about two drops per minute. Lubrication must have careful attention, because on it depends the preservation and good working of the pump.

*Feed Valves on the Supply Tank.*—There ought to be at least one valve open on the feed even when the pumps are stopped. When it is desired to change the boilers, first the valve of the new boiler is opened and the old one closed, or both operations may be done simultaneously. From time to time it is necessary to make sure that the valves fixed on the return stroke of the pumps on the cast-iron feed, and those placed on the reheaters, work properly. One should feel each shock which they produce, each pulsation of the steam pump. If it should be otherwise, in either case it would be a proof that it was fast and required inspection and cleaning.

*Heated Surface of Steam Boilers for Use in Extract Factories.*—The many years' experience of the authors, acquired in different tannin factories, enables them to affirm that the heating surface of the steam boilers is always represented by 5 square metres (54 square feet) in factories working by single effect and 4 square metres (43 square feet) in factories working by double effect—in both cases per metric ton of wood treated.

*Different Furnaces and Gas Generators. Bonnet-Spazin's Gas-heated Furnace.*—This system, shown in Fig. 78, is really a Fajje's furnace improved by the addition of an actual combustion chamber, of a front armature to regulate the heat B behind the Furnace A, and a manhole, G. If used to burn intractable fuel, such as exhausted wood chips or shavings from tannin factories, lignite, turf, etc., it must not be forgotten that the furnace in question is in reality a gas generator with its combustion chamber, its grate, and its systematic feed-hopper, E, through which is fed the intractable fuel to be burnt, which clearly shows that the system as a whole depends upon the distillation of the intractable fuel, so as to produce inflammable gases, which burn in this combustion chamber with an intensity which develops an amount of heat few furnaces of this kind produce, for it may be taken that 1 kilogramme of exhausted chips, with 60 to 62 per cent. of moisture, yields 1.4 kilogrammes of steam. This furnace, therefore, utilises wood to the fullest extent as it distils it the more perfectly. The working of it becomes rational only by excluding any addition of coal to the fuel, because such addition prevents the distillation by inducing the burning of the chips on the grate, and in the bulk of the



woody mass in such a way that a portion of the combustible gases are already burnt up prior to their entrance into the combustion chamber, thus diminishing the intensity of the heat on the boilers, to which this system of furnace is applied, by shortening the length of the flame, which ought to sweep half round the boilers. Besides, the use of coal induces the formation of clinkers which attach themselves to the grate, thus necessitating too frequent raking by the stoker, entrance of air, and all the other evils inherent to the use of any other fuel than spent chips in this special case.

Practically, this system of gas generator furnace requires for normal working 3.5 square decimetres of grate per square metre of the heating surface of the boiler, 3.5 square metres per 100

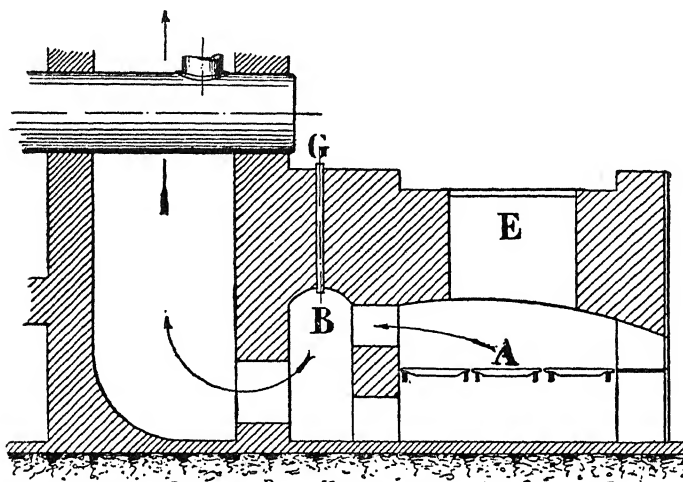


FIG. 78.—Bonnet-Spazin's gazogene furnace.

square metres of the heated surface. Moreover, it is necessary that in all the parts of the boilers the section of the flues should not be less than  $\frac{1}{4}$  to  $\frac{1}{3}$  of the surface of the grate.

*Working of Gas Generator Furnaces.*—If the masonry of the furnace be new it must be dried by keeping up a gentle wood fire for several days. Light the fire, working thus: Nearly close the main damper of the boiler to prevent too much draught. Spread on the grate a layer of readily inflammable fuel, shavings, paper, etc. Above this place a layer of well-dried twigs, and above this again some billets of dry wood. (In extract factories a stock of dry exhausted chips for use in lighting up and stimulating the combustion of the furnaces is always kept on hand.) The billets of wood may either be thrown in through the furnace mouth or through the hopper. When the grate is

charged the hopper is closed by an iron plate. Lay the fire on the lower bed in several places, simultaneously close the doors of the ashpit and open the furnace doors a little. Close the furnace doors when the whole surface of the grate is kindled and open those of the ashpit slightly. From time to time throw in logs of wood—always dry—as the previous ones are burnt, and so keep up the fire. This heating with wood is continued as energetically as possible until the arch of the furnace and the combustion chamber are at bright red heat. If need be the damper may be raised, but generally very little, to stimulate the combustion. When the combustion chamber is heated to quite its normal temperature one of the hoppers on the side is uncovered and charged with chips, care being taken to use rather dry chips. The fire is fed with chips through the first hopper and by logs through the others for about half an hour, and when the first hopper is alight the same procedure is followed with the other side hopper, then afterwards with the middle hopper if there is a third one on the furnace. When all the hoppers are filled with chips the main damper ought to be raised a little. The furnace is thus lighted up. The success of the operation depends especially on the heating of the masonry, which afterwards produces the distillation and inflammation of the chips. There need therefore be no fear in heating the furnace strongly before feeding it with chips.

*Rules for Working the Furnace.*—The chips should always cover the hoppers to avoid access of air through them. The chips should descend continuously and regularly. Care must be taken to ascertain from time to time that no arches or vacant spaces are formed to prevent their descent and that only wooden bars are used as pokers. The ashpit doors ought to be always more or less open, the furnace doors closed, the valves of the latter generally open, the inspection pipes generally closed. The speed of combustion is regulated by opening the damper, but in a general way it ought to be always slightly open. These rules are only approximative; they may vary with the draught of the chimney or the percentage of moisture in the wood. The inspection pipes ending in the combustion chamber indicate the intensity of the fire, and admit the complement of oxygen required for the ignition of the gas in this part of the furnace. When the grate is in good working order, which is especially the case on starting work, the damper should be opened very little, the flap valves of the furnace doors closed, and the ashpits only half opened, for if the combustion be too much stimulated on the grate distillation is too rapid and the gases do not become inflamed. When the grate becomes encrusted, the damper must be raised a little, the ashpit doors opened gradually to a greater extent, the flap valves of the furnace doors opened, and,

if necessary, one of the furnace doors is left ajar to admit air above the grate. This latter precaution is especially necessary when the grate is greatly encrusted. When the furnace is working well no smoke should issue from the furnace, and in the gas chamber the fire should be bright red, without flame or smoke. When it is necessary to stimulate the fire to get up pressure the poker or shovel is thrust underneath the fuel to remove the scoriæ which obstruct the entrance of air, and the main damper is raised a little.

*Night Fire.*—To keep the fire banked up during the night the hoppers must be well rammed with a wooden poker so as to press down the fuel as far as possible. It is then necessary to tramp with the feet on these hoppers and to make a heap above each, which is also trodden down under foot so as to pack the chips tightly. The damper is almost completely closed, but is so regulated that the smoke does not issue above the furnace. The furnace and ashpit doors are completely closed. The night-watchman ought to ascertain every time that he inspects the boilers that the furnace fire has not entered into combustion and that the steam pressure on the boilers has not increased. In the morning, to stimulate the fire, the main damper is raised to its normal height, the ashpits opened as customary, and the poker or shovel thrust under the grate to let the ashes fall which have formed during the night and block up the grate.

*Cleaning Out the Grates.*—The grate takes about eight or ten days to get dirty, so that complete cleaning need only be done after that interval has elapsed. This cleaning is done in sections, dealing for example with one hopper every four or six days. The cleaning is done as follows: The wood filling the hopper to be cleansed is tramped down so as to form an arch and stop the descent of the fuel; the fuel on the grate is allowed to burn out, which takes about ten minutes, and only the corresponding part of the grate is cleaned. During this time the descent of the wood through the other hoppers is forced a little, and as soon as the cleaning of the hopper is finished, the cleansed portion of the grate is covered with inflamed fuel from the neighbouring hopper; then when the fire has resumed its normal working the wood is made to descend as formerly through all the hoppers, poking through the arch formed in the beginning. It is necessary to select for cleaning a time when the pressure is high and the consumption of steam in the different departments of the factory is low.

*Cleaning of the Ashpit and the Heating Chamber.*—Every morning all the ashes in the ashpit must be removed. After clearing it out the small tub in the ashpit must be filled to the brim with water. This tub ought to be filled with water two or three times each day and night, so that the ashes may be

always drenched as soon as they fall from the grate. After each cleaning of the grate or part thereof the clinkers must be removed to the outside, and not piled in a heap in the heating chamber. This heating chamber ought always to be in good working order, and the gangway in front of the façades well cleared, so that the ashpit doors may be easily handled.

*Godillot's Furnace.*—For the combustion of intractable fuel such as spent tan or exhausted chips, the systematic combustion furnace of Godillot seems to the authors to be perfectly adapted. A summary description will, therefore, be given of this system, which has received numerous applications, both in tanneries and in the tannin industry. To realise perfect and hence economical combustion in a factory furnace, the amount of air required to burn the fuel must be brought on to the grate and spread regularly over it. It will be seen, therefore, that if it is desired to use such fuel as moist tan chips, impregnated with water or residuals from extract factories, the largest of ordinary grates are defective, each charge blocking up the interstices through which the air passes, and almost extinguishing the portions in ignition. Take as an example of the poverty of these chips the residue from the manufacture of chestnut extract. The chips, as they issue from the extractors, contain 66 per cent. of moisture and 34 per cent. of woody fibre, the calorific capacity of the woody fibre being half that of coal, 4000 calories instead of 8000, the 34 of woody fibre may be replaced by 17 of coal. This substance may, therefore, be compared to a fuel containing 17 of coal and 66 of moisture, or bringing the total to 100, 20 per cent. of coal and 80 per cent. of moisture. It will be seen that the ordinary grate is quite unfit to burn such fuel. Besides, intractable fuel is bulky. The following table gives an idea of the space occupied by each:—

TABLE XVII.—COMPARATIVE VALUE OF WASTE PRODUCTS USED AS FUEL

	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.
Moisture . . . .	68	52	62	40	55	60	14	12	29	65
Calorific intensity .	800	1400	1200	2000	1500	1100	3200	3300	2600	2600
Weight (kg.) of cub. met. . . .	500	330	500	300	150	200	260	140	260	600
Kgs. = 1 ton coal .	10,000	5700	6600	4000	5300	7300	2500	2400	3200	4500
Cub. met. = 1 ton coal	20	17	13	14	35	36	10	17	12	10

A, wet spent tan; B, drained spent tan; C, chips from extract factories; D, wet sawdust; E, wet bagasse (cane sugar); F, wet cane chips from diffusion; G, dry chips (oak); H, rice hulls; I, linen waste; J, peat.

The last horizontal line of the table shows the volumes in cubic metres equivalent to 1 ton of coal. Thus, to replace a ton

of coal, it is necessary to burn 20 cubic metres of wet spent tan, 35 cubic metres of bagasse, or 13 cubic metres of exhausted chips. To accomplish this result Godillot designed a pavilion grate in the shape of half a cone. It consists of horizontal, semicircular bars, the diameters of which decrease from base to summit. These bars overlap like the laths of Venetian blinds, so as to retain the finest particles, whilst allowing the necessary space for air to pass through. Hand stoking of these enormous bulks would be too severe a task. The mechanical stoking is done by means of a cast-iron helical screw with increasing

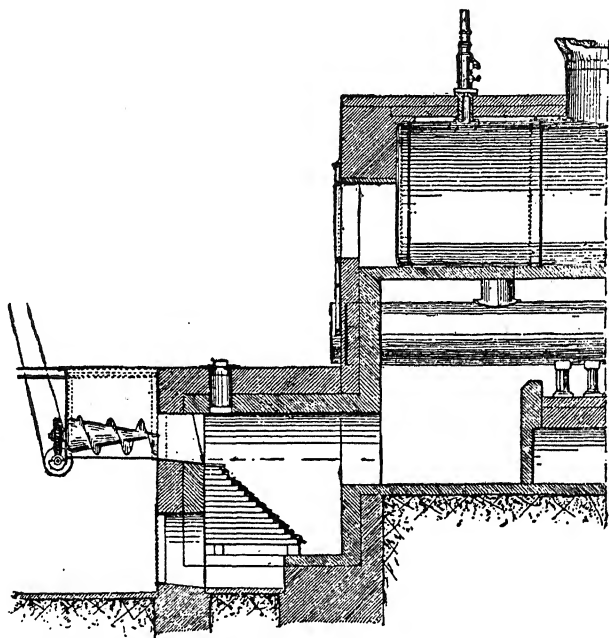


FIG. 79.—Godillot's furnace applied to a semi-tubular boiler.

"buckets" [expanding screw]. Woody fibre is in the form of irregular, filamentous fragments; spent tan and bagasse do not run readily, because the particles attach themselves to the threads of the helix and cannot get freed therefrom. The body of the helix, instead of being cylindrical is conical, and the point is directed towards the exit, so that the space between the threads of the helix shows an ever-increasing capacity. In this way the helix can draw along the material throughout the whole length of the hopper, at the bottom of which it turns. Fig. 79 shows the plant used by Luc and Patin, manufacturers of oak extract at Nancy, where chips are burnt containing 62 per cent.

of moisture. The substance to be burnt is run into the charging hopper; the helix, with increasing thread, brings it to the top of the pavilion grate; it dries, heats, inflames, descends on the slope of the cone in the form of a thin layer, in proportion as the fuel underneath is consumed; finally, it reaches the horizontal grate, where the combustion is finished, and where the ashes accumulate; they are easily withdrawn by the side doors provided for the purpose. The furnace works quite regularly. Luc and Patin's plant comprises seven furnaces, heating 500 square metres of heating surface; the economy realised is 18 tons per day.

One kilogramme of drained spent tan, with 55 per cent. of moisture, converts barely 450 grammes of water into steam, in ordinary plant, whilst in experiments made by M. Compère, engineer-director of the Parisian Association of Steam-boiler Proprietors, on Godillot's plant, 1700 grammes were generated. Godillot has erected a similar installation for six boilers, 500 square metres of heating surface, at the Gondola factory at Nantes, likewise for the Company of Fives-Lille, for the factory of Di Vono-Pringo (Java), for the factory of Trystam & Co. at Dunkirk, with the same success. The advantages of the plant are the following: (1) The raising of poor material to the rank of industrial fuel; (2) better combustion; (3) regularity in working, which avoids the risk of overheating and allows of a regular draught; (4) elimination of excess of air; (5) simplification in stoking; (6) complete prevention of smoke, even in the case of most intractable fuel.

*Chimneys. Brick Chimneys.*—There is an advantage in a tannery having a brick chimney lined at top and bottom; it should be furnished with a lightning conductor, and its interior fitted with access ladders, because this kind of industry does not require great regularity of pressure in the boilers, even if it utilises its spent tan as fuel, using a gas generator furnace, which requires a chimney section of 64 square decimetres or 900 millimetres diameter at the top per 100 square metres of heating surface of the boilers.

*Prat's Chimney with Forced Draught.*<sup>1</sup>—Extract factories, of which the output and the regular working of the manufacture are a function of the pressure of the steam, have a greater interest in installing a chimney with forced or mechanical draught, which consists in propelling into a special apparatus, termed "the pressure transformer," a current of air under pressure, generated by a fan, placed outside the circuit of the gases to be entrained, and which generates by its passage an induced current which entrains the combustion gases. This transformer

<sup>1</sup> Now advantageously replaced by Sturtevant's system.

may either be placed in the interior of the chimney, to increase the draught, which may be increased from 2 to 25 mm., or directly in the main flue, where the combustion gases join, where it then does the duty of the chimney. Fig. 80 shows in section the principle of this system, which has since 1896 received

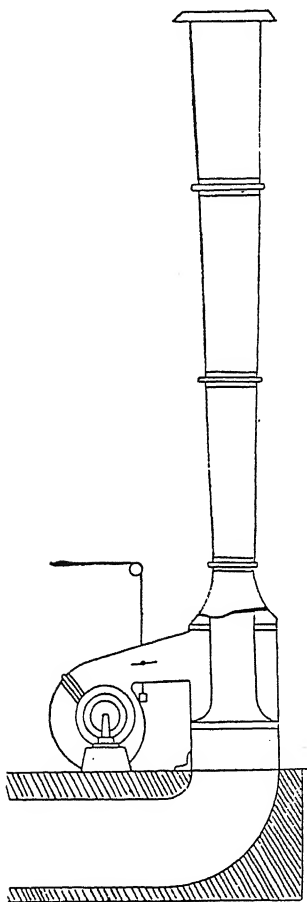


FIG. 80.—Mechanical draught applied to a furnace.

numerous applications, and which consists in the aggregate of: (1) a centrifugal fan (blower) placed outside the circuit of the combustion gases, so as to avoid simultaneously its destruction by sulphurous acid, or its encrustation by soot, and its heating by gases, generally at a high temperature; (2) a transformer of pressure forming a chimney; (3) a vent pipe, with regulating valve, connecting the ventilator with the transformer. These appliances, in view of their maximum utilisation, are calculated and constructed on a practical basis by which it is possible to obtain (1) a better yield of the pulsating fluid; (2) the free propulsion of the gases aspirated. It may be said that the draught in constant working, which can be realised with a motor power of about 1 per cent. of that produced by the boilers, by means of a simple fan placed outside the circuit of the combustion gases, with the pressure transformer adjusted to the orifice, in which it is to be used, and with the autovisible depression which results therefrom, has not only great aspiration capacity, allowing of its utilisation in all degrees of intensity of combustion, whilst rendering heating easy and economical, but it still further presents a real superiority over fans

which aspirate or directly propel the combustion gases. This system of draught by suction maintains its superiority, both as regards working expenses and general working, even over ordinary chimneys with natural draught. Thus it may be pointed out that an extract factory, treating 60 tons of wood per twenty-four hours, consequently requiring 240 square metres of boiler

surface and 8.4 square metres of grate (in the case of a gas generator furnace), will require a natural draught chimney of about 30 metres in height and 1.4 metres diameter (1.5 metres in section), which would be replaced by a chimney with mechanical draught on Prat's system of 10 metres in height only. In the case of a Godillot furnace (pavilion grate) and for a boiler of 100 square metres of heating surface, it is necessary to take 62 square metres of section or 800 mm. in diameter as the section to be given to the chimney.

*Steam Engine.*—It will be sufficient to point out that the choice of a steam engine in an extract factory is not of great importance, the waste steam being invariably and entirely utilised in heating the evaporation plant and for the concentration of the tannin liquors. Nevertheless, it will be well preferably to adopt a horizontal system, with condensation and expansion capable of being varied by the regulator, revolving at the rate of 60 to 100 revolutions; this arrangement allows in the first place of sure and constant working, at the same time that the facility of economic working may be by escape, or, if need be, by condensation. Figs. 81 and 82 shows Robatel, Buffaud & Co.'s type, of which the regular working, the solid construction, the simple management, the easy installation, and the low cost of maintenance, have caused it to be adopted in many factories.

*Steam Engines. Maintenance.*—Ascertain regularly on each occasion before starting the steam engines that no workman is engaged with the belts or shafting, and no tool or material of any sort that may cause an accident is in the way. Stop the steam engines preferably at the dead-point so as to have the piston rod completely out of the cylinder. To start an engine it is necessary: (1) To open widely the steam valve on the steam feed from the boilers, but very slowly, especially if the pipe is cold, so as to heat it gradually and avoid bumping of water; (2) bring the engine to the dead-point in front if it is not so already; open the blow-off cocks of the steam box and cylinder in front and behind; (3) open the steam valve on the engine to reheat and "blow-off" the rear part of the cylinder; (4) close the steam valve, turn the engine by hand to bring it to the dead-point behind, and again open the steam valve to heat and "blow-off" the front of the cylinder. During the time of heating the cylinder, fill the lubricator with oil, lubricate all the joints which only possess one lubricating hole and regulate the automatic lubricators with visible flow; (5) when the cylinder is completely warm and the lubrication finished, close the valve of the engine, place the latter by hand at its starting-point, that is to say, a little beyond one or other of its dead-points, and open the valve gradually until it is completely open in proportion as the engine attains its normal speed. Leave the blow-off



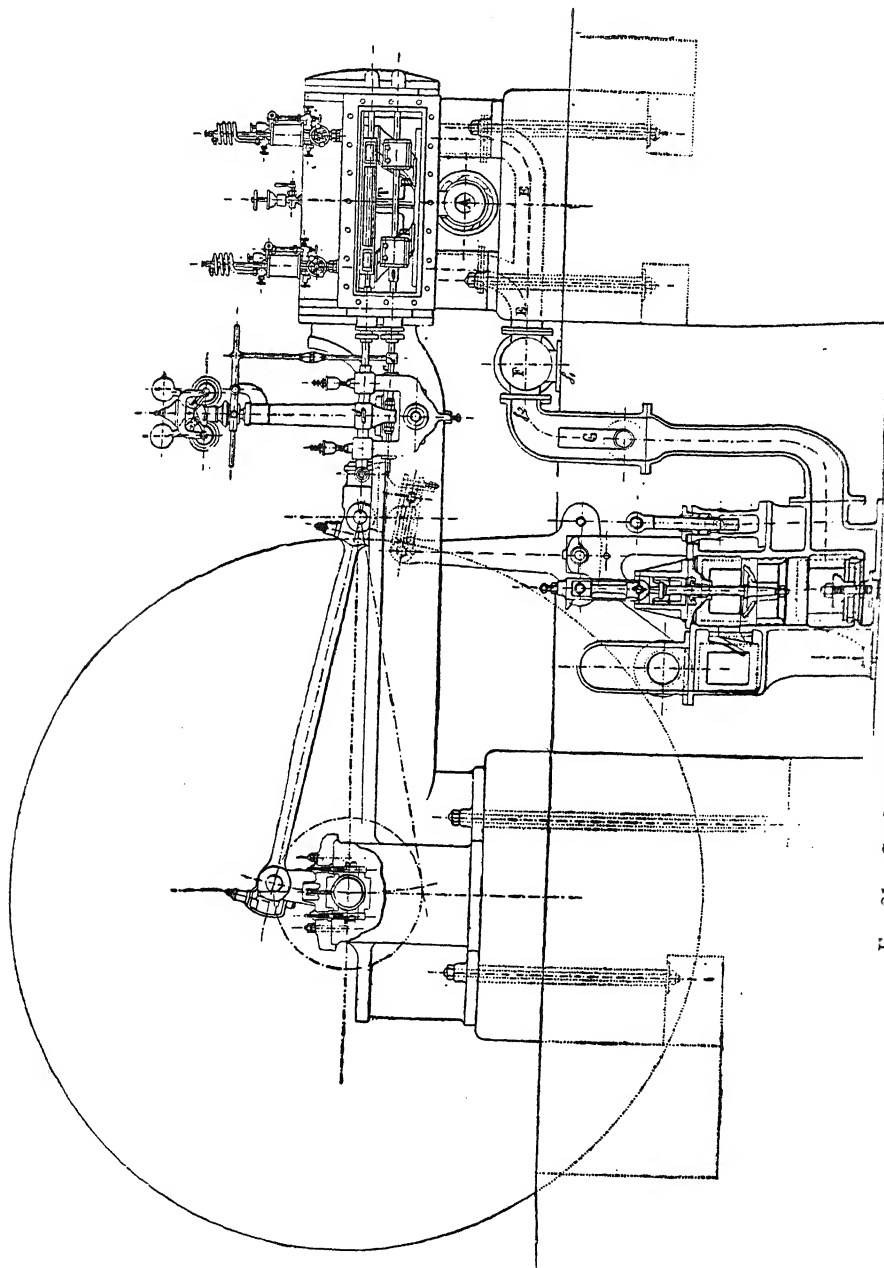


FIG. 81.—Condensation steam engine. Robatel, Buffaud & Co.

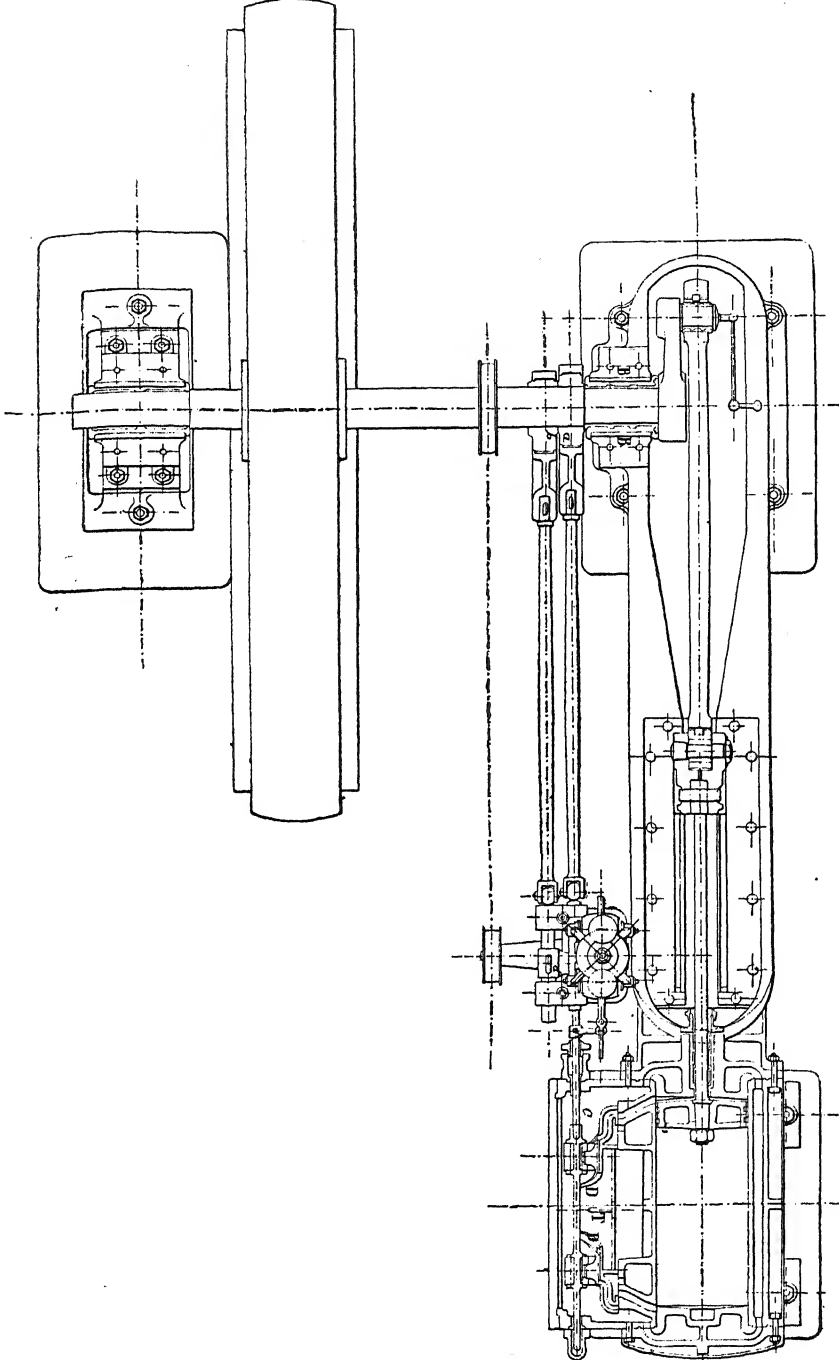


Fig. 82.—Condensation steam engine. Robatel, Buffaud & Co.

cocks entirely open for the first two minutes after starting, then close them. To stop an engine slowly, close the steam valve on the engine as well as the automatic lubricators. The engine ought to be stopped at one of its dead-points, preferably at the front one, and if it does not come into that position it must be brought so by hand. Ascertain before starting the steam engines that the butterfly valve of the escape is open to the free air if the evaporating plant is not at work. For lubricating the engines it is necessary to use valvoline for the cylinder and the draw box (a thick and black oil), and for the bearings, crank, eccentric, regulator, etc., machinery oil of good quality. Make sure always that the automatic lubricators work perfectly, and keep the glasses of the lubricators of the cylinders and of the draw boxes quite clean so as to verify always the flow of oil. Engines ought to be kept very clean, the polished parts cleaned every day, the rough parts well wiped. When the mechanic finds that one of the parts of the engine has become hot, he ought to force the lubrication of that part, watch it attentively, and if the heating persists advise the foreman, who will order, if need be, the stoppage of the engine and an inspection of the damage.

*General Shafting.*—The whole of the shafting should be lubricated every morning and evening. At each stoppage the shafting should be inspected to see that no bearing has become heated; as soon as it is perceived that one of the bearings has a tendency to become heated, it must be closely watched and its lubrication forced up to the next stoppage. If need be, stop at once and lift the cap to see that there is no obstruction on the bearing or the shaft; should there be any trace of obstruction, remove it immediately before starting again, and take care to clean the lubricators and then the lubricating holes and the little grease channels in the shaft cushions.

*Fixed Pulleys.*—In the case of all pulleys in two pieces make sure that all the pins are perfectly screwed to the block and that the collars have no play. If it be seen that any of the pins are unscrewed stop the shafting at once and rescrew these pins; rescrew the collars immediately if need be.

*Loose Pulleys.*—It is necessary when inspecting the bearings to inspect the loose pulleys at the same time and insert lubricant in their lubricator and see that they do not heat. If one begins to heat, the shafting must be stopped, the lubrication of that pulley forced and restarted. If the heating persists, which is a sign of obstruction, it is necessary to undo the shafting which carries this pulley; remove the obstruction, clean the lubricator, the lubricating holes, and the little grease channels of the locking ring.

*Piping and Taps in General.*—Each department where

steam is used having its special valve for drawing steam from the boilers, this valve should be perfectly open when the corresponding department is at work and completely closed when it is stopped. When the valve on the boilers is opened it must be done very slowly; first of all only run on a thread of steam to heat the pipes throughout its length, and gradually open afterwards to avoid all bumping, which would cause the joints to bump and the pipes to burst. All the valves and all the taps ought to be kept constantly in perfect working order, the stuffing boxes and the joints quite tight; all leakage ought to be noted

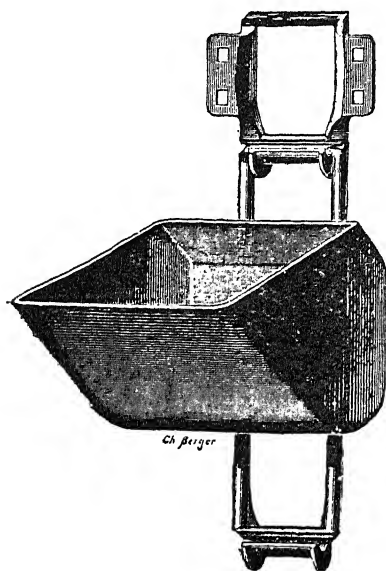


FIG. 83.—“Ewart's” chain.

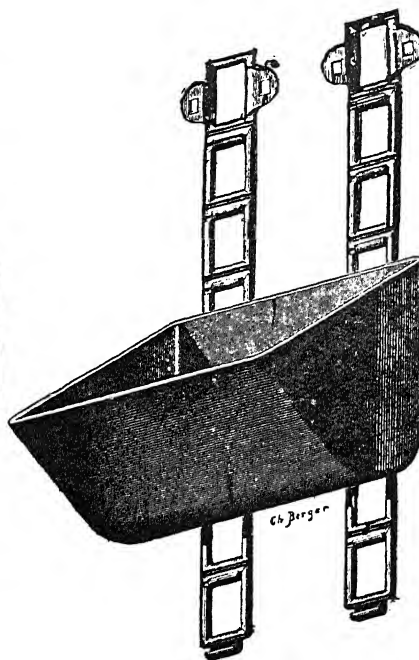


FIG. 84.—“Ewart's” chain coupled.

and repaired forthwith, however small it may be, as soon as it occurs. The joints of the pipes and the steam taps should be made with best quality of sheet-rubber of 4 to 5 mm. thick with brass-wire gauze insertion. The packing of the glands of the valves and taps ought to be made with a layer of asbestos of the desired size, and these glands ought to be packed as little as possible, only enough to prevent any escape of steam. Take care in all the taps to screw the pins of the glands very equally so as not to wedge them.

*Elevators and Conveyers. Ewart's Chain Elevator.*—This system consists (Figs. 83 and 84) of links which may be coupled

together and detached at will. The links are generally rectangular, three of the sides being cylindrical, and the fourth consisting of a hook. This chain is of malleable cast-iron, of quite a special quality; all the links are rigorously calibrated, and consequently interchangeable, which assures regular working, along with the greatest facility for elongating and shortening the chain at will without loss of time. Although Ewart's chain is made of metal, it is not, for equal effort, heavier than a belt; in many cases it may even be of less weight.

*Harrison's Chain System.*—Harrison's chain consists of closed links and open junction links. Fig. 85 sufficiently shows the

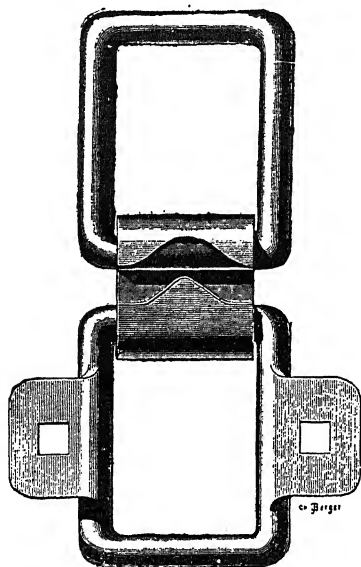


FIG. 85.—"Harrison's" chain.

method of connecting up the chain. Like Ewart's chain, Harrison's steel chain is applied to elevators, conveyers, etc., but it is more particularly adapted for plant that has to do heavy work, or where the conditions of resistance of cast-iron would involve the use of two coupled Ewart chains, or at least a strengthened and consequently heavier chain. Harrison's chain was first made of cast-iron, but the simple and regular form of the links led to its manufacture in cast-steel, which has placed it in the first rank of chains with detachable links. At the present day the firm of Burton Fils, of Paris, who are specialists in this branch of construction, manufacture this chain in stamped steel,

which still further increases its durability and its resistance to rupture.

*Plummer Blocks. Cast-iron Feed Receivers.*—Figs. 86 and 87 show these accessories which complete with the chains and the stamped sheet steel cups the whole elevator shown in Fig. 88.

*Conveyers.*—These appliances, which generally receive the chips of wood or ground bark from the elevators, consist of an endless cotton band, of dimensions corresponding to the capacity of the elevators, passing over two rolls, or steel drums, the one a transmitter of speed, the other a receiver, and of some inclined rolls along the length so as to guide the edges of the band. A conveyer may also be fitted with a movable truck, which en-

ables the chips or bark to be discharged, at any point of the wood granary in extract factories, or in the warehouse for crushed bark in tanneries. Figs. 89 and 90 show these two applications.

*Chip Granary.*—The men allocated for filling autoclaves ought to use every effort to conduct the operation as rapidly as

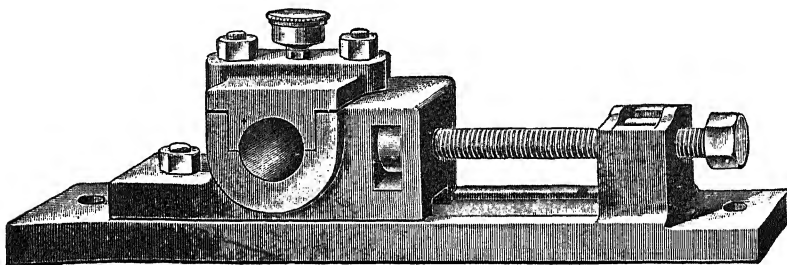


FIG. 86.—Plummer block.

possible; they should begin to shoot the chips as soon as the signal is given by the battery foreman. During the time which elapses between the two charges their work is to accumulate as much wood as possible on the aperture of the autoclave. The chips must not remain more than three or four days in the granary, as they are liable to ferment; it is necessary therefore

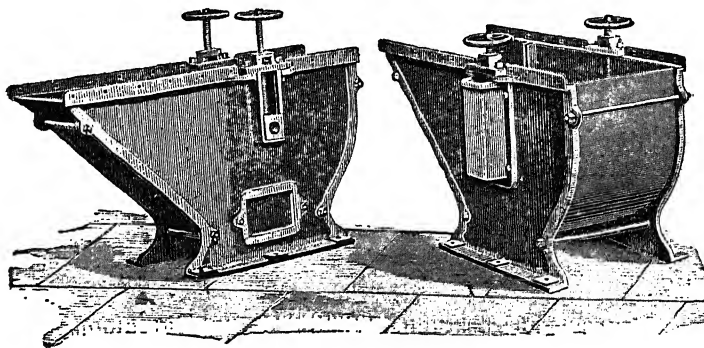


FIG. 87.—Cast-iron receiver.

to empty this granary every four days, at least, by collecting together all the chips from the far corners. The men ought to remove carefully all pieces of iron, large or small, which may be mixed with the chips. No piece of iron, however small, should ever enter into the autoclaves.

*Cutters.*—Only such industrial machines will be mentioned as are of great capacity, and consequently those having a speed

of 350 to 450 revolutions a minute, slow-speed cutters (100 revolutions a minute) with a long passage and mechanical pusher being now almost completely abandoned, as absorbing much of the motive power, in consequence of the pressure of the log against the sides of the boss, thus playing the part of a real brake, without any compensation in the output. It may be added that for the same amount of power expended a cutter

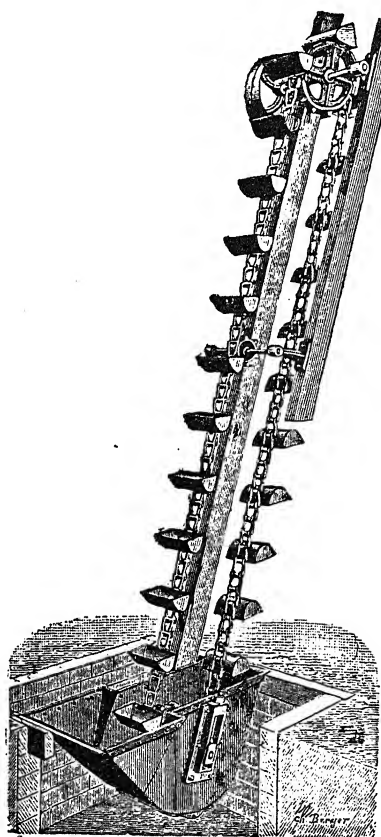


FIG. 88.—Elevator.

with an angular boss of great speed, such as that shown in Fig. 91, has an output twice as great as that of the cutter with mechanical pusher. The high-speed cutter of great capacity is moreover very simple (see Figs. 91 and 92). Its parts are reduced to: (1) One angular boss of cast-iron 700 to 800 mm. in diameter fitted with two apertures or bays for receiving the steel knives or blades, the number of which varies according to the

capacity of the cutter, and which are fixed by means of pins or gudgeons reinforced by screws; this part of the construction ought to be sufficiently strong to stand any test. (2) One steel shaft traversing the centre of the said boss on which it is

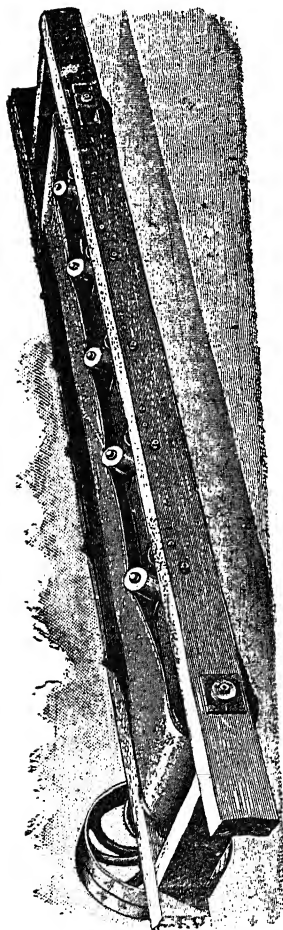


Fig. 89.—Conveyer.

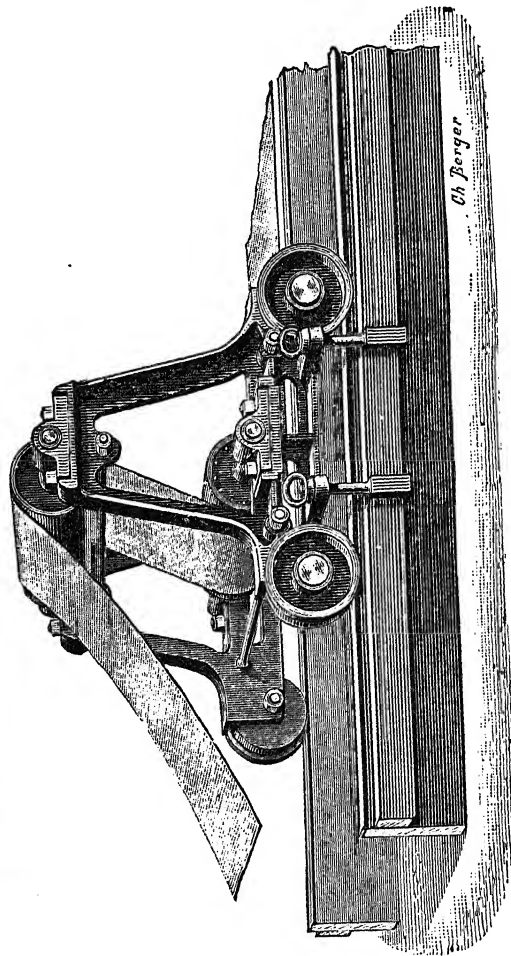


Fig. 90.—Portable truck of conveyer.

strongly fixed. (3) Three lubricating bearings with bronze cushions. (4) One inclined cast-iron trough for reception of the logs, and its spur or anvil which assumes the shape of the angle of the central boss thus facilitating the cutting. (5) Two pulleys loose and fixed.<sup>1</sup> (6) One cast-iron fly-wheel, the whole

<sup>1</sup> Unless Burton's gearing be used.



protected by a hood of steel plate and mounted on three oak beams, tied and bolted, which rest on a concrete foundation, at the bottom of which is a pit for receiving the chips and into which dips the cup elevator previously described. A cutter capable of dealing with 2250 kilogrammes (2½ tons) per hour of logs 25 cm. (10 inches) square absorbs 20 to 25 h.p. In normal working the log once placed in the sufficiently inclined chute ought to be drawn mechanically by the blades of the boss. The workman in charge of the cutter should be solely engaged in feeding in new logs as fast as the others are "swallowed".

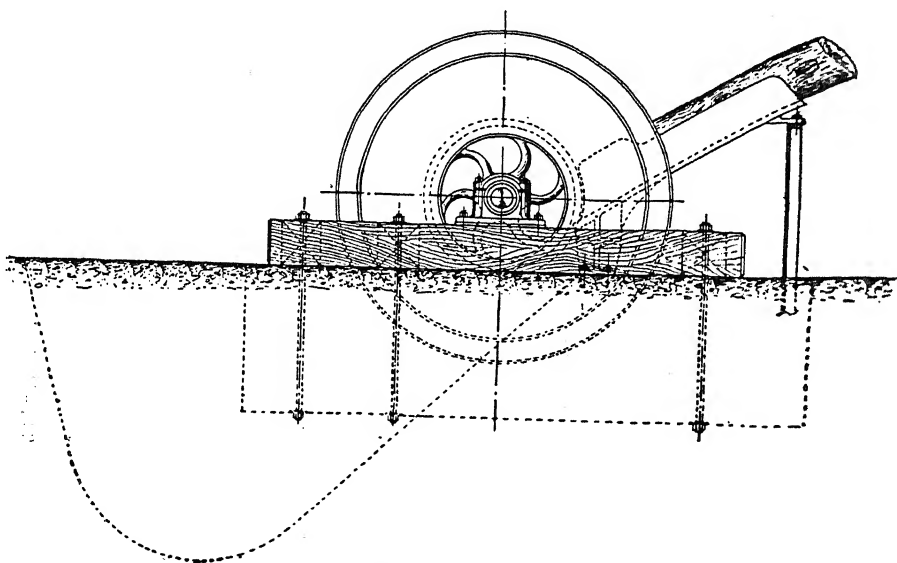


FIG. 91.—Cutter of great capacity.

Chopping machines and bark crushers need only be mentioned in passing, the systems being numerous and described in several works on tanning<sup>1</sup> and the illustrated catalogues of constructors of tannery machinery, such as Blair, Campbell & McLean, Huscam & Brown, Lennox Foundry Co., etc.

*Instructions Regarding Cutters and Elevators. Starting.*—Before starting a cutter see that there is oil in the three bearings. Begin by starting the elevator. This operation requires a man to put the belt on the elevator and another at the cup chain; the latter ought to pull on the chain, especially if there is wood in the bottom pit, which is liable to block the cups, thus causing the belt to slip and burn. The cutter is then

<sup>1</sup> *La Tannerie*, L. Meunier and C. Vaney, 1903.

started, by slowly pushing the belt off the loose pulley on to the fixed pulley.<sup>1</sup> The belt must be brought into gear gradually. Before placing the logs of wood in the cutter, it is necessary to see that the boss has attained the right speed, and that the elevator has completely emptied the pit of chips. When such is the case, the cutter may be fed with logs. As far as possible, large logs should be alternated with small ones. If, owing to the large size of a log, the speed of the cutter slackens, it is necessary to wait until it has regained its speed before running in the next log. During working, if the elevator stops it is necessary to immediately cease feeding the cutter with logs, and

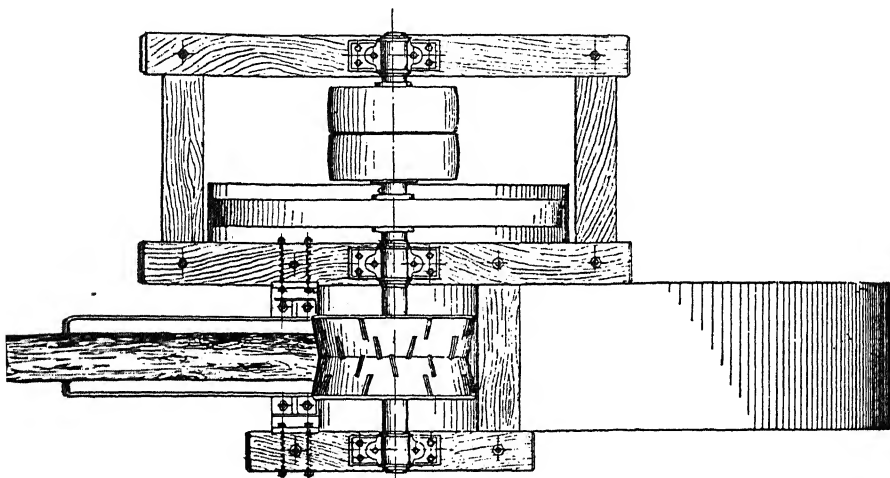


FIG. 92.—Cutter of great capacity.

not to restart the elevator until after the cause of its stoppage has been ascertained. If need be, inform the foreman.

*Stopping.*—To stop work, first cease feeding with wood, take the belt out of gear, leaving the elevator at work until it has emptied the pit of chips. In the interval clean up around the cutter, and remove the chips projected therefrom or which have fallen from the elevators. Then bring the elevators out of gear. No chips must be thrown into the pit when the elevator is not at work.

*Lubrication and Heating.*—Oil must be run into the lubricators of the bearings at least every two hours, and it must be ascertained frequently during working that the bearings have no tendency to abnormal heating. If one of the three bearings, particularly the central one, becomes somewhat hot with a

<sup>1</sup> It is better to use friction gearing.

tendency for this to increase, it is necessary to lubricate freely at first; stop the cutter a moment to allow the bearings to cool, and restart.

If the heating still continues it is a sign of obstruction. The cutter must then be stopped, the shaft disengaged from the heated bearings, and the cushions of the bearings scraped with the scraper on the parts which are scratched. Likewise polish the part of the shaft which rests in the bearing, to remove any trace of obstruction. Carefully clean the lubricators and put back the shaft in its place. Run the cutter empty for, say, half an hour, and do not insert any wood until it is seen that no fresh heating occurs. At each stoppage of the shafting of the cutters it is necessary to give a screwing-up turn to the lubricators of the loose pulley, and fill these lubricators with special lubricant every day.

*Sharpening the Knives.*—The knives should be sharpened very uniformly, so that the cutting edge is perfectly straight and set square on the side.

*Inserting and Adjusting the Knives.*—The knives ought all to be inserted in the same way and they all ought to project 4 to 5 mm. from the central boss. It is necessary to use the special gauge prepared for the purpose and to follow it very exactly. Take care to screw up very tightly the bolts which fix the knives.

*Regulating the Spur of the Chute.*—The spur ought to be securely bolted to the chute, and the position of the latter may be varied by screw bolts fitted to the cross beam of the building. This position must be so adjusted that the play between the spur and the central boss is 7 to 8 mm. quite uniformly throughout all its length. When the feather edge of the spur is rounded by the friction of the wood, it must be redressed to bring the feather edge to a sharp angle. Such work is done with a graving tool. When, by repeated dressing, the spur is shortened to such an extent as to leave only 7 mm. (0.275 in.) of play between the central boss and the spur, the latter must be changed.

*Extraction. Diffusion Plant. Wooden Vats.*—The tannin industry, which in the beginning used wooden vats as extractors, could profitably use them still for the three reasons previously given: A good yield, easy clarification and cheap decolorisation, high strength in tannin. As to durability, pitch-pine vats with staves 78 mm. (3 inches) thick will last as long as copper autoclaves. The authors have handled vats of this kind which, after fifteen years' use, and being taken down and displaced three times, continued to be used for the safe extraction of sumac and mimosa without their tightness being in any way affected. Did not the Gondolo Factory, a firm of reputation,

start with wooden vats? a certain arrangement of which vats was the subject of their patent (*brevet*) of 2nd June, 1880. Besides, this important factory, which treated as much as 300 tons in twenty-four hours, possessed numerous batteries of wooden vats to do the work of which the catalogue of plant and equipment of 1903 again makes mention. At the present day, five French factories and some foreign ones still use, with success, this rational form of extractors. The authors recommend this system, so much the more because, installed according to their instructions, it presents all the advantages of a battery of copper autoclaves. The factories which make extracts other than chestnut have every advantage in the exclusive use of wooden vats (except their intrinsic value) without any of their disadvantages, and for the following reasons: (1) With a battery of wooden vats certainly no more steam, but probably less, is used than with a battery of autoclaves. (2) The battery of wooden vats has the advantage over copper vessels of being absolutely safe. (3) The installation of a battery of wooden vats costs much less for initial expenditure and requires less repairs than a battery of autoclaves, because the pressure on the latter demands special and costly piping which soon leaks. (4) The management of a battery of wooden vats, although more onerous than a battery of autoclaves, is simpler and more systematical. (5) The yield per cent. on the wood treated in extract of 25°, obtained by the use of wooden vats, is equal if not superior to that furnished by a battery of autoclaves. (6) In open vats heated to 100° C. the juice or liquor obtained is less coloured and contains less insolubles (consisting of particles of wood mechanically entrained, pectic and resinoid bodies), consequently is more quickly clarified and more readily decolorised afterwards than in the case of juice or liquors extracted under pressure in the autoclaves. (7) Finally, and what is the most important point, after having demonstrated the superiority of extraction in open wooden vats, this system yields extracts with a high percentage of tannin, which always exceeds by 2 per cent. that of extracts obtained by extracting the wood in autoclaves, the temperature, a function of the pressure, which in such plant reaches 1.5 kilogrammes (equal to 127° C.), destroying a notable quantity of tannin. In this connection it will suffice to place, in parallel, the table summarising the experiments of Professor Eitner, an authority on the subject, whose results fully confirm our assertions. The substances experimented on were placed in an autoclave and submitted for two hours to temperatures of 120° C. (248° F.) = 1 atmosphere; 133° C. (271.4° F.) = 2 atmospheres; 151° C. (303.8° F.) = 4 atmospheres; 164° C. (327.2° F.) = 6 atmospheres. The results of these experiments are given in Table XVIII., which shows in A the amount of dry

TABLE XVIII.—EITNER'S EXPERIMENTS ON THE EXTRACTION OF TANNING SUBSTANCES AT DIFFERENT PRESSURES

	A. Extract per cent.				B. Tannin.				C. Non-Tannin.			
	Pressure. <sup>1</sup>				Pressure. <sup>1</sup>				Pressure. <sup>1</sup>			
	1.	2.	4.	6.	1.	2.	4.	6.	1.	2.	4.	6.
Barks: 1. Pine .	29.06	32.76	31.54	30.72	16.24	12.92	8.58	6.49	12.82	19.82	22.96	24.23
„ 2. Oak .	22.14	23.79	23.88	24.04	11.07	7.99	5.62	3.22	13.07	15.80	13.26	20.82
„ 3. Cajota .	40.54	41.41	38.14	26.88	21.45	21.45	11.41	2.27	18.79	20.00	21.73	24.11
„ 4. Mimosa .	42.10	45.00	48.52	41.83	31.61	30.75	29.98	26.60	10.49	13.54	14.25	14.73
„ 5. Hemlock .	13.70	14.07	13.73	12.70	9.30	8.34	4.50	2.13	4.40	5.73	8.20	11.60
„ 6. Willow .	9.16	14.95	17.49	19.39	4.80	3.16	1.59	1.59	6.0	10.15	15.90	17.80
Myrobolams .	41.73	44.19	45.88	44.12	25.02	23.02	14.52	12.49	16.12	21.17	31.46	31.63
Algarobillas .	68.62	63.06	49.25	48.85	36.44	24.04	8.37	8.47	32.18	39.04	40.88	40.38
Divi-divi .	69.40	64.72	55.90	46.56	45.12	33.14	18.08	14.93	24.28	31.58	37.26	31.63
Valonias .	49.23	50.70	47.79	41.45	29.97	27.28	24.78	18.92	19.26	23.42	23.41	22.53
Galls .	45.24	43.87	41.43	39.90	29.32	27.08	23.78	17.73	15.92	16.78	17.65	18.25
Sumac .	43.38	52.33	51.10	47.48	22.85	22.70	11.27	8.87	20.53	29.63	39.83	39.61
Oakwood .	9.76	10.96	23.60	24.81	6.44	6.50	5.52	2.57	3.32	4.46	18.08	22.34
Quebracho .	23.91	24.38	25.39	26.23	21.05	21.50	18.42	13.60	2.86	2.88	6.96	12.63
Tannin .	100.12	100.59	100.16	92.79	94.76	85.55	63.49	39.14	5.46	15.04	36.67	53.05

extract per 100 parts of tanning material examined; in B the proportion of tannin contained in this dry extract, and finally in C the proportion of non-tannin in the same residue. It follows from these experiments (1) that the strength of the extract, which increases from 0 to 2 atmospheres with about two exceptions, decreases afterwards in the greater number of cases or maintains its strength between 2 and 4, to fall very greatly between 4 and 6 atmospheres. (2) In all cases the tannin per cent. of substance treated lowers rapidly in passing from a pressure of 1 to 6 atmospheres. (3) Between 1 and 2 atmospheres, and consequently between 120° and 133° C. (248° to 271.4° F.), the decrease in tannin is generally quite small, especially with cajota and mimosa bark, oak and quebracho woods, but with algarobilla, divi-divi, and myrobolams the loss in tannin is considerable. (4) The non-tannins of Column C always increase with the pressure, owing, on the one hand, to the transformation of tannin into non-tannin, and, on the other hand, to the solution of these bodies owing to their hydration.

Entrusted with starting a chestnut extract factory in Le Gard, in bringing the daily production from 2500 kilogrammes (2½ metric tons) to 6500 kilogrammes (6½ metric tons) of ex-

<sup>1</sup> In atmospheres.

tract of 25°, the authors determined the difference in tannic strength of two extracts which were then manufactured. The one, from a battery of six open wooden vats, showed an average of 30 to 31 per cent. of tannin, determined during the course of manufacture extending over a period of more than a month, and an average daily production of 2500 kilogrammes (2½ metric tons) at 25°; whilst the battery of autoclaves, in which the pressure oscillated between 0·5 and 1 atmosphere, the daily production of which reached 4000 kilogrammes (4 metric tons) of 25° extract, never exceeded an average of 28·5 per cent. of tannin. In fact, according to numerous analyses made on the two qualities of extracts, a minimum difference of 2 per cent. has always been to the credit of that made in open vats. These industrial experiments, based on the above data, enable the authors to maintain their preceding conclusions without fear of contradiction.

*Battery of Wooden Vats.*—Fig. 93 shows the authors' arrangement for a battery of sixteen wooden vats of 12,000 litres (2640 gallons) capacity and capable of containing 3 metric tons of wood, answering, therefore, all the requirements of rational extraction. In this system the heating surface required for the boilers will always be taken as 4 square metres per ton of wood treated in a factory possessing a triple effect; that is to say, that possessing such an installation, not even 1 kilogramme of coal will be burnt, but there will be an excess of chips sufficient to light the furnaces after any stoppage, say weekly, for example. This battery is furnished with its piping and connections, which enable it to work rationally with the facility of isolating each vat. The transference of the juice or liquors is effected either by the weight of these pumped into an elevated vat, *i.e.* by gravity, or by means of a bronze centrifugal pump<sup>1</sup> connected to the vats by two collectors, one for discharging, common to the transfers, and the other for filling, common to the water feed. Each vat is also fitted with appliances for steam heating, and with two bronze discharging cocks; the top is covered with a lid with a chimney for the evacuation of mud, and finally with a special water-level. The lower part of each vat has a double bottom and an arrangement for constant circulation, so as to accelerate maceration by the rapid movement of the slices from top to bottom.

*Open Copper Pans.*—The authors prefer pitch pine for economical reasons, otherwise copper vessels may be substituted, but as there is no industrial advantage, the subject need not be dwelt upon further.

*Copper Autoclaves or Extractors.*—Practically, an extract

<sup>1</sup> Limb's dynamo pump.

factory can work with an extraction battery, consisting of four, five, or six autoclaves, the useful capacity of which is generally from 10,000 to 11,000 litres (2420 gallons), that is to say, capable

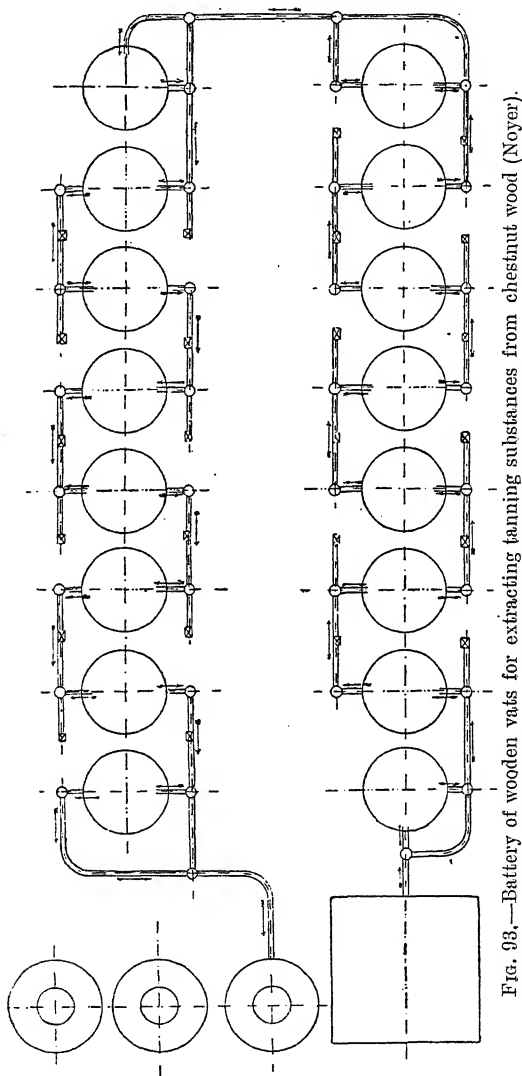


FIG. 93.—Battery of wooden vats for extracting tanning substances from chestnut wood (Noyer).

of holding  $3\frac{1}{2}$  to 4 metric tons of wood chips, and yielding 5500 to 6000 litres (1210 to 1320 gallons) of liquor. It may be stated once for all that a tannin concern, to be of any im-

portance at the present day, must treat at least 60 tons of wood per day.

*Arrangement of the Battery.*—Fig. 94 shows a battery of five autoclaves with their feed water, steam, and juice pipes, as well as their taps; they are all adapted for the maceration of chestnut, and in the case of a battery of six autoclaves the sixth isolated is used for the direct extraction of quebracho or other mixed extract, which will be readverted to in Chapter VII. (Quebracho Extract). These autoclaves of the capacity above mentioned have the following dimensions: total height 4.6

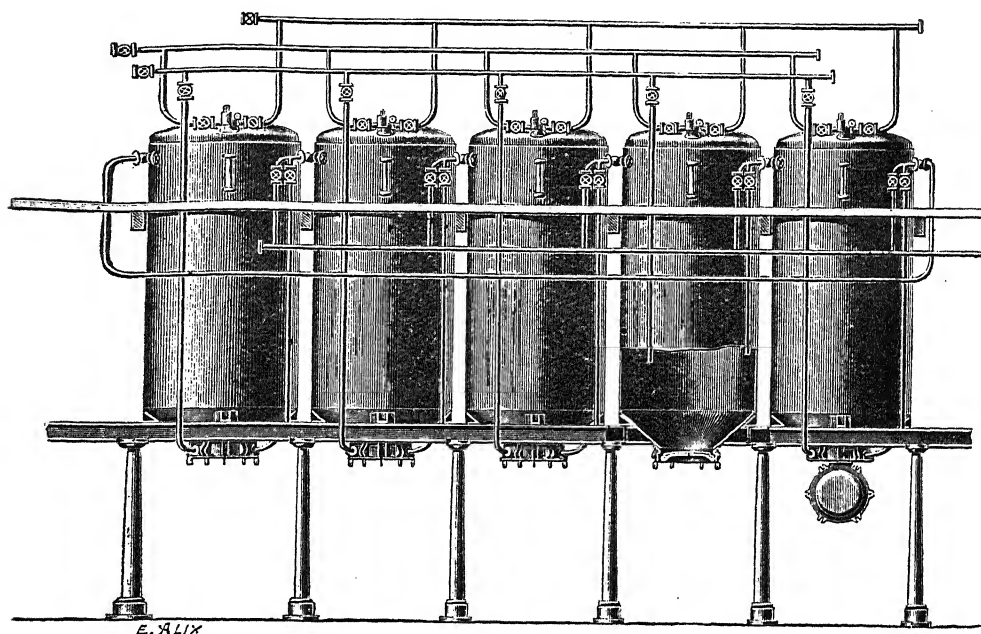


FIG. 94.—Battery of five copper autoclaves for extracting tanning substances from chestnut wood, etc.

metres, height of the cylindrical part  $3\frac{1}{2}$  metres, exterior diameter 1.85 metres. The thickness of the copper plate of which they are made is generally from 8 to 9 mm. Per day of twenty-four hours fifteen to sixteen autoclaves are emptied; after deducting from the time required for boiling that occupied in cleaning and in charging an autoclave, there remains fifteen to twenty minutes as the actual time of decoction of the charge of chips in an autoclave. This work is intensive, and the authors in no way recommend it, because the rapidity of the operations is such that it involves a pressure which reaches 2 kilos. per sq. cm. in almost all the factories which use



it, and because it then fatally induces the drawbacks already mentioned. Thus, a factory treating 60 tons of bark in this way will give a yield in liquor of 3·8°, barely exceeding 1350 litres (297 gallons) per ton of wood treated, corresponding, with the loss inherent to this method of manufacture, to a maximum yield of 19 kilogrammes of 25° extract per 100 kilogrammes of dry wood (40 to 45 per cent. water).

*Routine to Follow in Managing the Autoclaves in Intensive Working, with Five Waters giving Nine Washings.*—The five autoclaves being supposed to be numbered 1 to 5 in such a way that the communicating pipes are arranged from 1 into 2, 2 into 3, etc., 5 into 1, each autoclave is successively emptied in the order of these numbers. If the series of operations be taken up at the moment when one of the autoclaves is being discharged, No. 2 for example, the following is the condition in which the extractors should be found: No. 1 full of wood and liquor from 5. No. 2 empty of both wood and liquor. No. 3 full of wood and liquor from 2. No. 4 full of wood and liquor from 3. No. 5 full of wood and liquor from 4. In the battery all the taps without exception are closed, except, perhaps, that of the steam tap of No. 3, if the water be not sufficiently hot, and if the pressure has not yet reached 1·5 kilos. per sq. cm. The following is the order in which the operations to the number of 12 succeed one another: (1) Fill 2. (2), (3), (4), (5) Pass 1 on 2; 5 on 1; 4 on 5; 3 on 4. (6) Fresh water on 3. (7) Discharge by the collector of 2 as soon as the feeding of 3 is finished. (8), (9), (10), (11) Pass 1 on 2; 5 on 1; 4 on 5; 3 on 4. (12) Empty 3; fill 3. These twelve operations are performed thus:—

(1) *Filling Extractor No. 2.*—Close the lower manhole. Feed in the wood by the top manhole. During this time apply a little steam to pack the chips, turn off the steam when it escapes with force from the top manhole. Finish filling the extractor and close the top manhole.

(2) *Running the Liquor from No. 1 on to No. 2.*—In extractor No. 1 the pressure should be 1 to 1½ kilos. per sq. cm. Open the steam escape tap of No. 2 to allow the air to escape. Open communication between No. 1 and 2. The liquor flows from No. 1 into No. 2, its level rises in the pipe and reaches its normal height, which shows that the transfer is finished. It is necessary to complete the amount of liquor by borrowing from 5 to balance the suction produced by the new wood. Close the communication tap. Close the escape. Apply heat by turning on steam, the pressure rises, and when it reaches 1½ kilos. per sq. cm. = 127° C. (260·6 F.), turn off steam.

(3) *Passing Liquor from 5 on 1.*—This is done whilst No. 2 is being heated. It is carried out in the same way as No. 1 on No. 2.

(4) and (5) *Passing Liquor from 4 on 5 and of 3 on 4.*—As above.

(6) *Feed in No. 3 with Fresh Water.*—Communication tap closed. Steam tap closed. Escape valve open. Water tap open. Fill with water to 10 cm. below the top of the water-level and close the water supply tap. Apply heat by turning on steam and raise the pressure to  $1\frac{1}{2}$  kilos. per sq. cm. =  $127^{\circ}$  C. ( $260.6^{\circ}$  F.). Turn off steam at the moment this pressure is reached.

(7) *Discharge by the Collector of Extractor No. 2.*—This operation is done as soon as the feeding with water of No. 3 is finished. In this extractor the pressure ought to be 1 to  $1.5$  kilogrammes. Open the communication tap on the collector. The juice is propelled into the liquor vat. Close the communication tap.

(8), (9), (10), (11) *Passage of No. 1 on No. 2, No. 5 on No. 1, etc.*—These passages are effected as above.

(12) *Emptying of Extractor No. 3.*—Its liquor has just been passed into No. 4. The communication tap is closed as in all the others. The pressure is still  $0.5$  kilo. per sq. cm. Purge the lid of the discharged manhole by the tap. Completely open the steam escape. The pressure falls, and when it is at 0 open the top manhole, then open the discharge manhole. Strip and discharge the wood. Open the upper tap even before the pressure reaches 0; the steam remaining in the extractor facilitates the opening. All the operations of charging and discharging should not take more than twenty-five minutes with experienced men (with extractors of 10 cubic metres capacity). The starting-point being again reached it is the turn of No. 4 to be discharged, and the extractors are in the following condition : No. 1 full of liquor from No. 5. No. 2 full of liquor from No. 1. No. 3 empty of wood and liquor about to be charged. No. 4 full of wood and liquor from No. 3. The liquor is about to be passed again and it will be filled with fresh water before being discharged. No. 5 full of liquor from No. 4. Operations recommence in same order changing by one unit the order of the vats, the fresh water always being run on to the vat next to be discharged. The liquor which has just been passed over fresh wood is sent to the collector, *i.e.* to the liquor reservoirs. This is the liquor which indicates  $3^{\circ}$  to  $5^{\circ}$  Beaumé. To pass the liquor the condensation tap is opened and also the escape of the extractor which receives it, the communication and the escape are closed. Steam is turned on, and turned off when the pressure reaches  $1.5$  kilos. per sq. cm., not to be again opened until the next passage. The liquor is thus heated each time it changes extractors.

*Intensive Working with Seven Liquors.*—In this case it will

suffice if the battery be fitted with two collectors: the water, common to the juice, and the steam, so that the normal routine of working will be that indicated by the following table:—

TABLE XIX.—SCHEDULE SHOWING ROUTINE WORKING OF EACH CELL IN DIFFUSION BATTERY DURING PROGRESS OF TANNIC ACID EXTRACTION

Routine of Working.		Duration.	No. of Autoclave.	Titre of the Liquor.
Vol.	Water on No. 7 . . .	...	...	...
	Passed . . .	...	...	...
	Under pressure . . .	...	4	...
Titre	To pass on No. 6 . . .	...	...	...
	Passed . . .	...	...	...
Vol.	No. 6 under pressure . . .	...	...	...
	To pass on No. 5 . . .	...	5	...
Titre	Passed . . .	...	...	...
Vol.	No. 5 under pressure . . .	...	...	...
	To pass on No. 4 . . .	...	1	...
Titre	Passed . . .	...	...	...
Vol.	No. 4 under pressure . . .	...	...	...
	To pass on No. 4 . . .	...	2	...
Titre	Passed . . .	...	...	...
Vol.	No. 4 under pressure . . .	...	...	...
	To pass on 3 . . .	...	3	...
Titre	Passed . . .	...	...	...
Vol.	No. 3 under pressure . . .	...	...	...
	To pass on No. 1 . . .	...	4	...
Titre	Passed . . .	...	...	...
Vol.	No. 1 under pressure . . .	...	...	...
	To be elevated . . .	...	5	...
Titre	Elevated . . .	...	...	...

By adopting the method of working given in the preceding table, it will be seen that the relation existing at the moment of the charge of the new wood is 2, 4, 6 figures, representing the second, fourth, and sixth boiling, waiting until the first boiling be on new wood. At that moment the relation is 1, 3, 5, 7 figures, representing first, third, fifth, and seventh boiling, the last which precedes the discharge of the chips from the autoclave, which have been exhausted seven times. Working thus, any number of boilings may be made, but the defect of superheating always occurs at the moment of the passages (transfers), and the pressure registered by the manometre reaches  $1\frac{1}{2}$  kilos. per sq. cm. =  $260.6^{\circ}$  F. With this method of working, and if a reasonable number of autoclaves be stripped in twenty-four hours, whilst exhausting to one-tenth the tannin contained in the wood, 22 to 23 per cent. yield is easily obtained with dry wood (40 to 45 per cent. water), corresponding to 1650 litres (363 gallons) of liquor of  $3.8^{\circ}$  per ton of wood treated.

TABLE XX.—SHOWING EXHAUSTION OF CHESTNUT CHIPS BY CONSECUTIVE WASHINGS

Liquor.	A. <sup>1</sup> Tannin per cent. in different Liquors passing successively through Chestnut Wood Chips.	B. Of 100 parts of Tannin dissolved the different boilings remove the following.
1	3·8	43·37
2	2·05	23·44
3	1·23	14·04
4	0·83	9·47
5	0·42	4·79
6	0·35	3·99
7	0·08	0·90

Hence seven washings suffice. Supplementary washing continued on the seventh liquor, eighth liquor 0·003 per cent., ninth liquor 0·02, which shows that working with eight waters, and *a fortiori* nine, is useless in commercial extraction.

The exhausted chestnut chips, as they come from the autoclaves, contain 65 to 66 per cent. of moisture, that is to say the chestnut wood treated containing 50 per cent. of moisture absorbs, by maceration, an additional 15 to 16 per cent. of water; that is the percentage they contain when burned in the gas generator furnace, to the total exclusion of any other fuel, for the production of the whole of the steam for an extract factory. At certain factories endeavours have been made to dry the chips by means of a cylindrical mechanical drier, the principle of which is that of the automatic stage furnace for pyrites, utilising the heat lost by the furnaces, which removes from the wood about 40 per cent. of water; this system being adopted, the perpetual motive power absorbed (12 h.-p.) and the initial expense, which is considerable, are not compensated for by the removal of the 40 per cent. of water contained in the exhausted chips, seeing that simple gas generator furnaces are in existence, requiring no motive power nor great maintenance expenses, utilising this poor fuel in its ordinary wet condition, and yielding 1 to 4 kilogrammes of steam per kilogramme of chips burnt. On the other hand, industrial tests made with a view to the utilisation of such wood waste for the manufacture of acetic acid and methyl alcohol have not given and cannot give any good results, because these chips must perforce be dried and yield a lower result than ordinary wood when distilled for acetic acid and methyl alcohol. Those who erected plant after the patents of Treber, Trocknung or Fischer soon came to the same conclusion; the authors have, likewise, made numerous industrial

<sup>1</sup> Industrial experiments made on mixtures of equal parts of barked Dauphiné, Vivarais, and Lyonnais wood and on important lots of Gard wood.

experiments on the utilisation of this wood waste for the manufacture of paper, none of which led to any satisfactory result.

*Different Systems of Autoclaves.*—Figs. 95 and 96 show the different forms of autoclaves in use in extract factories; that of

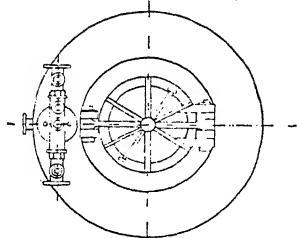
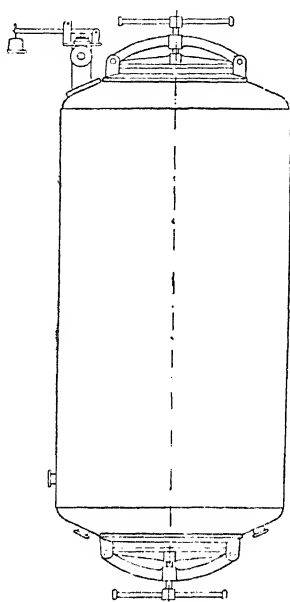


FIG. 95.—Autoclave with stamped bottom.

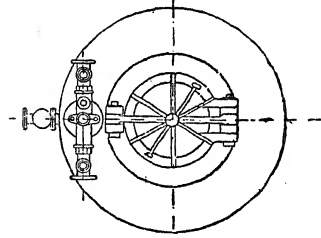
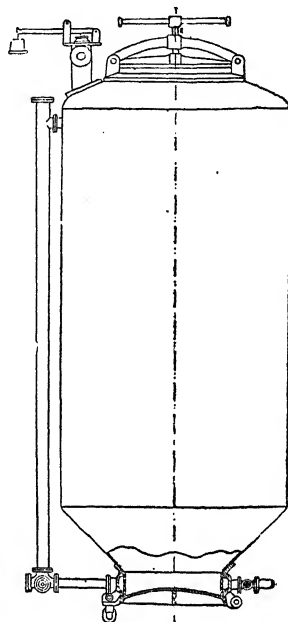


FIG. 96.—Autoclave with truncated bottom and Bonnet Spazin's arrangement.

Fig. 96 is the most generally employed, because it presents with its truncated base and its circular-fringed collarete in bronze, with manhole of 800 mm. diameter, useful advantages, which the authors themselves have confirmed in a factory of which they were the advisers. These various apparatus are evidently constructed all in bronze and copper as regards the parts in

contact with the juice, the armatures, the hinges, and the support for closing the manholes being of steel or wrought iron.

*Condensing Reheating Reservoir, J. Noyer's System.*—As to the successive escapes of steam from the autoclaves at the moment of transference, it is advisable to condense this steam, so as to return to the maceration the whole amount of condensed

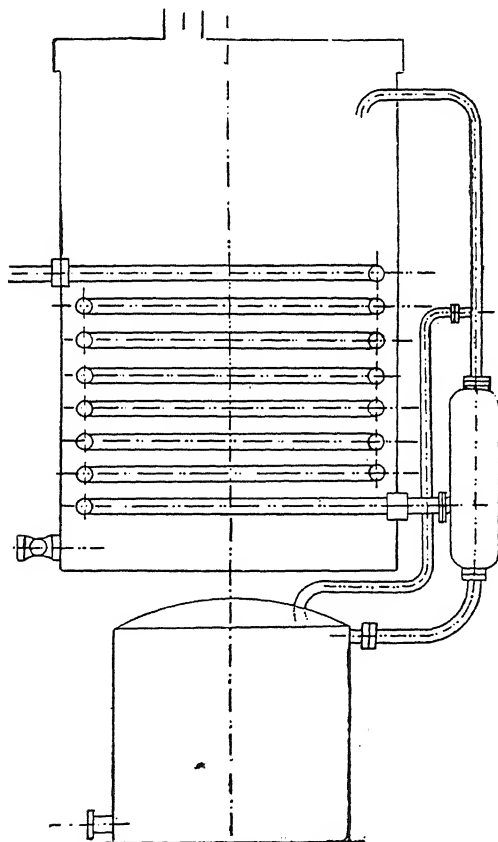


FIG. 97.—Reservoir condenser with coil, old system.

water. In place of the old system (Fig. 97), which consisted in passing this escape steam through a coil, immersed in the tank, which fed the autoclaves, the authors have installed their system shown in Fig. 98. It was designed because industrially, and especially in this case, condensation by a worm is materially imperfect, seeing that steam at 1.5 kilos. per sq. cm. is forced to condense rapidly when passed through a coil continually immersed in hot water, the spirals being always more or less

encrusted, therefore an enormous surface of coil is required, which in the case of a 60 ton factory would have a condensing surface of more than 21 square metres (some constructors count 0.35 square metre per ton of wood treated, which is quite insufficient), even this amount would not be enough because 10 per cent. of the steam would escape through the roof as loss

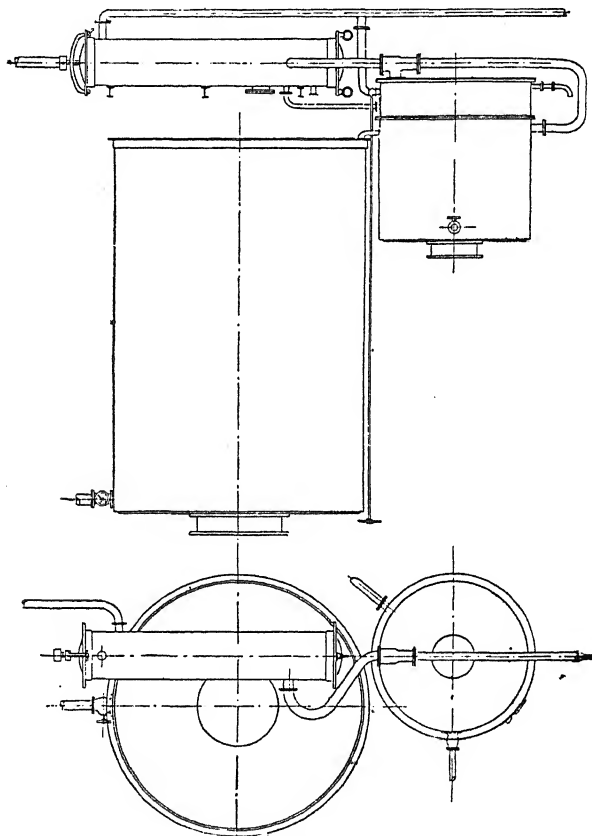


FIG. 98.—Reservoir-condenser-reheater (Noyer).

(without taking into account the damage produced by such projection, which always contains a fine spray of the tannin liquor). Moreover, the surface, owing to the amount of steam to be condensed, requires a large quantity of cold water and is even then never properly utilised. On the other hand, the escape of this steam through a coil occurs spasmodically, and wears it through rather rapidly; it also requires frequent cleaning in order to retain its maximum condensing surface; thus

it is that for many reasons the authors have established and applied in three French factories their system of condensing-reheating-reservoir, the use of which has given full satisfaction. The plant (shown in Fig. 98) consists of a tubular reheater, the capacity of which is based on the size of the extract factory, but which should not, in any case, exceed 10 square metres. It is, moreover, fitted with branch pipes, which connect it, on the one hand, with the escape collector of the autoclaves, and on the other hand, with the condenser-reservoir properly so called, consisting of a copper beck with calandria, on which an emulsifier of the author's construction is fixed, the whole being about 1000 litres (220 gallons) capacity. This plant, so fitted up, is placed at the upper level of the feed tank, into which the condensed water runs. To show the advantage of this installation, it may be stated that in addition to the water, which it heats from 95° to 98° C. (203° to 208·4° F.) and which not having been in contact with the open steam may be used to feed the boilers, it condenses almost entirely the whole of the escape steam from a battery of autoclaves of 60 tons capacity, the condensed water from which amounts to 12,000 to 14,000 litres (2640 to 3080 gallons), which again re-enter into the maceration work with a complement of ordinary water which exactly serves for the proper condensation, by emulsion, of the escape vapours, without fear of counterpressure or of the return of water to the autoclaves. All the pipes and manholes can be dismantled easily and quickly for inspection or cleaning, without any stoppage of the factory, thus keeping the condensation capacity of the plant constant.

*Liquor Tank.*—Whether a battery of wooden vats or autoclaves be used, the chestnut juice or liquors are propelled from these vessels, through a special collector, to a copper tank called the "liquor tank," the useful capacity of which fully represents the volume of a vat or an autoclave, and the bottom of which is placed about the upper level of the batteries so that the juice or liquor flows to the refrigerators by gravity.

*Cooling of the Juices or Liquors.*—An important point in the manufacture of extracts is the cooling of the juice or liquors (the temperature of the cooled juice should never exceed 18° C. (= 64·4° F.). Some factories do not use enough water for this purpose or do not utilise it in a rational manner. On the other hand, the temperature of the water often exceeds 18° C. (64·4° F.), the maximum adopted by the authors, which is a satisfactory one, as the liquors can always be cooled to about this temperature; it enables the condensed water to be utilised for the condensation of the steam from the evaporating plant. As the amount of cold water fit for condensing the steam from the evaporation plant is always appreciably one and a half times



greater than that required for the total refrigeration of the juice, it follows that the temperature of these juices approaches that of the initial water, because this traverses the refrigerators before being used for such condensation. The important point is to keep the tubular bundles forming the refrigeration system in a thoroughly clean condition, the best position for them being the vertical (Fig. 99); the upper rim ought to be about 500 mm. above the highest level of the extraction vats so that no pumping is necessary, every facility should, however, be provided for cleaning any of the parts composing the refrigerating system at a moment's notice.

*Tubular Refrigerators.*—As this treatise must be kept within a practical scope, dealing only with the latest and most improved systems in use, it is unnecessary to describe obsolete refrigerators, with vertical or horizontal coils, often immersed in a tank, in which the condensing water circulated, or in a channel serving the factory, because such a vertical or horizontal condition is always incompatible with frequent cleaning or control. The practical impossibility of obtaining good results with such systems lies in the fact that the deposits of mud and encrustations formed inside and outside of the tubes forming the serpentine cannot be cleaned when at work, nor are they removed by the steam which is passed through on stopping. These deposits lower its capacity by 50 per cent., and lead to non-utilisation of the condensing surface.

Only the refrigerating plant which appears up to now to have given the best results (see Fig. 99) as much from the point of view of refrigerating capacity, under the smallest volume, as that of easy cleansing of the tubular bundles of which it is composed will be described. As the figure shows, these refrigerators are vertical and consist of five elements with tubular bundles, the interior condensing surface of which is calculated according to the quantity of juice to be cooled from 100° C. to  $n$  degrees ( $n$  being the temperature of the cold water used by the factory). For normal refrigeration, *i.e.* under the above-mentioned conditions, and to cool the liquors from 100° C. (212° F.) to 18° or 20° C. (64·4° or 68° F.), supposing cold water at that temperature is available, according to the authors' experience, 1·2 to 1·5 square metres of condensing surface is required per ton of liquor at 100° C. (212° F.). The following are the differences in temperature observed with a liquor passing through five elements after issuing from the liquor vat where its temperature is 100° C.: At the first condenser 92° C. (197·6° F.) at the second 40° C. (104° F.), at the third 27° C. (80·6° F.), at the fourth 19° C. (66·2° F.), at the fifth 15° C. (59° F.). The water used for this refrigeration was at 15° C. and was afterwards utilised for the condensation of the steam of a triple effect of 150 square metres.

*Filtration Decantation of Juice.*—The cooled juices, as they come from the refrigerators according to the quality of chestnut extract to be manufactured, are filtered directly through filter presses, shown in Fig. 100, or by decantation through wooden or copper vats, the capacity of which reaches 200 to 500 hectolitres (4400 to 10,000 gallons). The filter presses most suitable for this purpose are provided with chambers with interposed

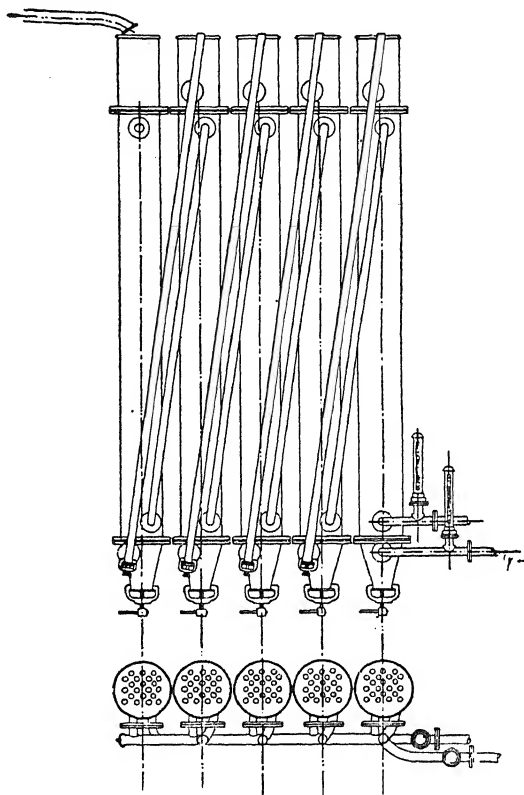


FIG. 99.—Tubular refrigerators.

wooden frames 800 mm. square (about  $31\frac{1}{2}$  inches), thirteen chambers and twelve interposed frames. A cotton cloth, of a special texture, separates the chamber from the frame, and exposes about 73 square decimetres of filtering surface, equal to 10 square metres, for the whole of the plates in such a press. On an industrial scale, and observing the working manipulations incidental to the management of such plant and the washing of the cloths, their output is 110 litres (22 gallons) of clear filtrate per hour per square metre of filtering surface, starting with crude

juice, cooled to about  $16^{\circ}$  C. ( $60.8^{\circ}$  F.), taking into account the stoppages and startings after the cleanings, which are required every four or five hours according to the quality of the wood treated. By this process pasty cakes are formed, which fill the interposed spaces; these consist of wood dust, mechanically

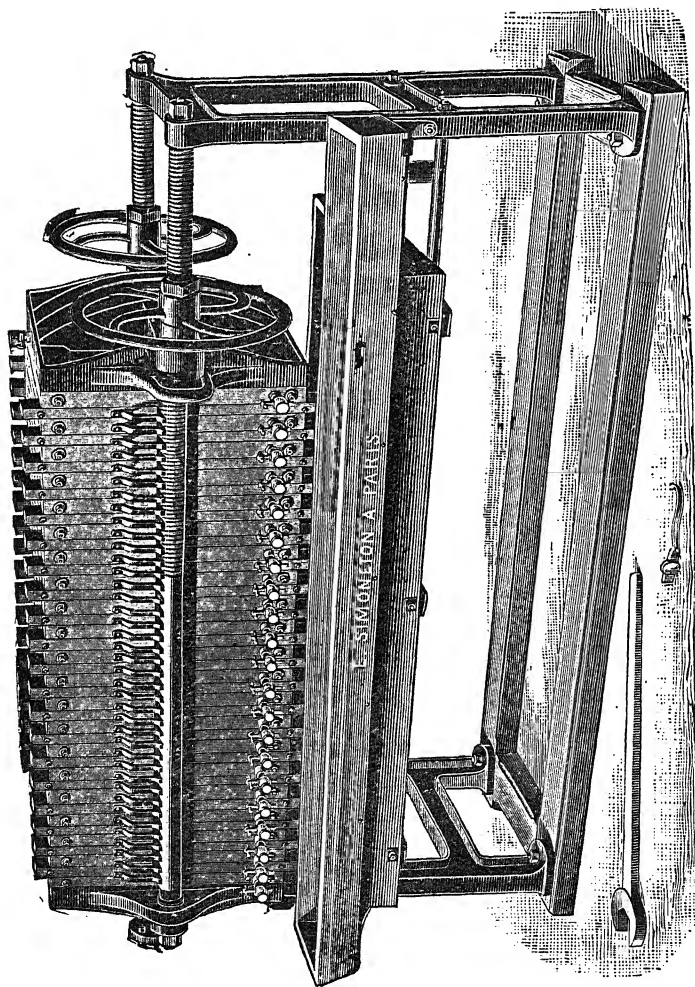


FIG. 100.—Filter press with interposed frames for the mechanical filtration of tannic liquors.

suspended, and of pectous and resinous bodies. The juice or liquors thus treated are freed from a large amount of insoluble matter, which enables chestnut extracts of  $25^{\circ}$  or  $30^{\circ}$ , almost entirely soluble in cold water, to be obtained, which are perfectly satisfactory for tanning purposes. The cakes, whether pasty or

compact, containing 6 to 7 per cent. of tannin, are again treated in a vat with hot water (open steam coil); yield liquors of 4° to 5° B., which, concentrated to 20°, yield gallic acid for dyeing. The original juice or liquors leave 1 to 1½ per cent. of cake, which, treated as above, yield 20 per cent. of their weight of gallic acid at 20°, leaving at the bottom of the vat in which they are treated a blackish, semi-hard, resinous mass, which amounts to about 20 per cent. of the cakes.

*Mechanical Clarification.*—Although clarified liquors yielding extracts soluble in the cold are obtainable by filtration, it is, none the less, a fact that this method of clarification is rather costly, owing to the motive power required for the pressure pumps and the working expenses (four men for two filter presses, clarifying 50,000 litres or 11,000 gallons of liquor), and especially the wear and tear of the cloths; the authors have tried to employ in place of such plant a decanting centrifugal, the principle of clarification of which is based on well-known principles. This system has already been tested and exhibited by La Société Civile des Études sur la Fabrication Perfectionnée des Extraits Tanniques (French patents, No. 161,958 and 165,140, 1884) the results not being at all satisfactory the style of working the authors believe being but little adapted to the nature of the liquid to be clarified; moreover, the apparatus used was not continuous, hence the output was insufficient. The authors having taken up these experiments from a different point of view, adopting the arrangement shown diagrammatically in Fig. 101. With this apparatus the industrial output per hour was 1000 litres (220 gallons) starting from cooled and decolorised liquors (immediately after treatment) or 600 litres (132 gallons) of clarified juice from decantation mud which fully justified their expectations.

From the above results, the authors are assured that this interesting problem is practically solved, and for this purpose they used the decanting centrifugal of Robatel, Buffaud & Co., the Lyons constructors, who built up a reputation for this sort of speciality, which the authors have been very pleased to utilise for the clarification of tannin liquors, using their special arrangement by which alone this object can be obtained.

*Decantation in Vats.*—The method of clarification in vats, which is still in general use at the present time, consists simply in collecting the cooled liquors, decolorised by nitrate of lead, or by blood, or by some other process, in large vessels containing 200 to 500 hectolitres (4,400 to 11,000 gallons) capacity and allowing them to settle therein, for several days, before concentration in the evaporation plant. During the interval, which varies with the process adopted and the routine of each factory, the chestnut liquor frees itself by precipitation, or coagulation,

of the colouring principles, pectous and resinous substances together with some tannin, which are deposited in the state of mud at the bottom of the vats, the volume of this precipitate is considerable and may amount to as much as one-fifth or one-sixth of the liquor decanted. Thus, by the nitrate of lead process, a vat containing 20,000 litres (4400 gallons) of liquor of 4° B., after four or five days of decantation, will yield 4000 litres (880 gallons) of sludge. Although a battery of vats may be arranged so as to simplify the decantation process and the filtration of the muds, this style of working will always be decidedly inferior to the mechanical filtration of the juice just described. Finally, it may be added that practically on an average 4 to 5 cubic metres of vat must be provided for every ton of wood treated to realise

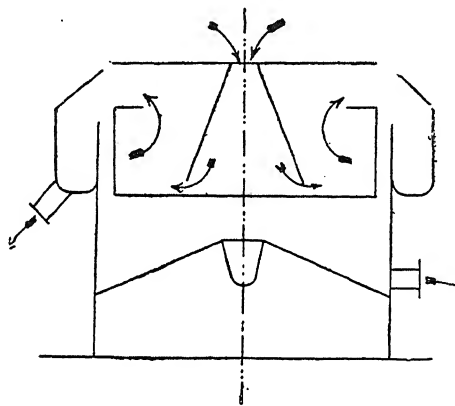


FIG. 101.—Decanting centrifugal for clarifying tannic liquors.

an efficient decantation. Some extract factories send these muds back indefinitely to be worked up in the maceration, etc., but this method of recovering the tannin contained therein cannot be too severely criticised. The disadvantages incidental thereto are far from being compensated for by the saving which is supposed to be realised by this recovery: (1) Because the extract corresponding thereto so produced escapes control. (2) Because these sludges contain so many impurities that it would not be wise to return them to the maceration; the liquors so obtained being rendered indefinitely impure. They thus require a larger amount of decolorising agent, they are more difficult to clarify, and they yield extracts of mediocre and irregular quality. (3) The piping through which the liquor circulates is rapidly encrusted and obstructed. The authors, therefore, in order to overcome these disadvantages, and at the same time

to obtain the quintessence of the juice contained in the sludge, recommend mechanical filtration.<sup>1</sup>

*Mechanical Filtration of the Sludge.*—In two extract factories which already possessed a battery of decantation vats, to avoid the injurious and indefinite reworking up of the muds, the authors had occasion to solve this problem by mechanical filtration, using the system of filter presses described under the filtration of the crude cooled liquors. By observing the same details, a good result is certain to be realised, averaging 25 litres (5½ gallons) of clear filtrate per hour per square metre of filtering surface. In this case the yield obtained by the filter press is one-fourth that obtained in the filtration of the crude cooled liquors; this is explained by the difficulty of filtration in the latter case; the percentage in cakes from the mud is 10 per cent. whilst it is only 1 to 1½ from the crude liquor. Nevertheless, although this yield appears small compared with that from the crude juice, it is worth considering when we find that 100 kilogrammes of mud yield 90 kilogrammes of clear liquor and 10 kilogrammes of cake. By this treatment there is almost a maximum utilisation of these residues, which embarrassed and still embarrass certain factories. If the cakes, whether pasty or consistent, are not treated, as previously indicated, for the extraction of gallic acid, they are then dried on trays over the boiler flues, so as to utilise the waste heat of the furnaces or gas generators burning exhausted chips. These cakes contain about 80 per cent. of moisture in their pasty state; in the dry state they contain only 5 per cent., and may be burnt in admixture with the spent chips. In a sample of cakes from filtration of the mud from juice decolorised by nitrate of lead, there were found on analysis 5½ per cent. of lead and 5 per cent. of moisture. An experiment for the complete drying of cakes already partly dried showed that they contained 70 per cent. of combustible matter.

*Data Summarising the Foregoing Facts as to the Filtration of Liquors and the Treatment of the Cakes.*—Weight of crude juice filtered per hour per square metre of filter area, 110 kilogrammes. Weight of crude mud filtered per hour per square metre of filter area 25 kilogrammes. Cake in crude juice, 1·5 per cent. Mud in crude decolorised juice, 20 per cent. Clear liquor in mud, 90 per cent. Cake in decantation mud, 10 per cent. Moisture in pasty cakes, 80 per cent. Dry cake in

<sup>1</sup> The authors add that for public health reasons and to avoid river pollution or the inconvenience of neighbours, tannin factories should discontinue any discharge of residues or residual waters, more or less contaminated with tannin and unfit for vegetation, when they do not contain organic matter from the treatment of the liquors by blood or some chemical reagent. The authors assert that in a factory using their new processes these disadvantages do not occur.

pasty cake, 20 per cent. 20° gallic acid in pasty cakes, 20 per cent.

*Mechanical Clarification of Sludge.*—Finally, and according to the indications given above, the authors estimate that the mechanical clarification of sludges, by means of the decanting centrifugal, indicated by the diagrammatic representation in Fig. 101, is preferable to any other, and for the same reasons which apply in the case of the filtration of the juice. Moreover, the yield in clarified juice is 600 litres (132 gallons) per hour with less labour and less wear of the cloths, because the said apparatus works by centrifugal force, so that the formation of cakes takes place on the circumference of the copper basket, and because the clarified liquor is decanted as a continuous jet by the upper portion of the same basket. The following are the advantages which accrue by adopting it in a factory treating 60 tons of wood with a volume of liquor amounting to about 90,000 litres (19,800 gallons) in twenty-four hours: (1) Four appliances of 1·200 metres in diameter of this nature will replace a decantation battery of 5000 hectolitres (110,000 gallons). (2) The four decanting appliances require only 30 square metres of surface, whilst the decantation battery requires 300 square metres. (3) The approximate cost of four decanting appliances amounts to 16,000 francs (£640), whilst a decantation battery costs 35,000 francs (£1400) without including the cost of construction of the building in which it is to be located. (4) The liquors being clarified as soon as cooled or treated, may be concentrated immediately; one is not, therefore, dependent on the decantation tanks, which necessitate a constant reserve and storage of the juice which is, especially in summer, essentially liable to fermentation, with consequent loss of tannin.

*Decolorisation. Different Processes.*—The (French) patents relating to tannic acid taken out since 1879 form a long series; recourse has been made to numerous substances as decolorising agents.

These processes are not necessary in the manufacture of good extract, as the tannery can, and should, restrict itself to deliveries more or less in accord with its system of tanning; extracts decolorised in so many different ways are no guarantee to the tanner using them, after frequently having had mishaps often due to them alone. In support of the foregoing, it will suffice to point out the loss in extract, and consequently in tannin, which results from the decolorisation of liquors by the "blood" process (one of the most rational) and which, in the same way as in the clarifying of wine, carries down along with the tannin the pectic, resinous and colouring substances contained in the liquor; thus 40,000 kilogrammes of liquor treated with Bourgeois' solution of blood at 6·5° B. (7·5 kilogrammes per

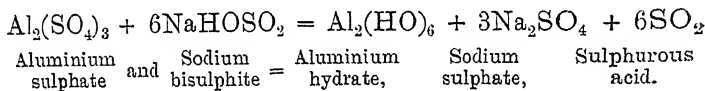
TABLE XXI.—CHRONOLOGICAL LIST OF REAGENTS PATENTED IN FRANCE AS TANNIC LIQUOR DECOLORISERS

	Year.	Patent No.	Decolorising Agent.
1	1880	136,046	Sulphurous acid and bisulphites.
2	1879-82	130,625 } 223,951 }	Blood or albumen.
3	1883	155,842	Oxalic acid and alumina.
4	1883	157,153	Animal charcoal.
5	1884	161,433	Haloid or oxygenated salts with mineral or organic acids.
6	1884	155,026 cert. add.	Sulphurous acid gas under pressure.
7	1884	163,189	Aluminium hyposulphite.
8	1884	163,521	Barium chloride.
9	1886	174,972	Casein with prior treatment of wood by sulphuric or hydrochloric acid.
10	1886	56,304	Lead nitrate.
11	1899	290,159	Lactic acid.
12	1895-97	242,041 } 269,628 }	Dregs of wheat, barley, maize or rice, oil cake.

1000 kilogrammes of liquor at 4° B.), which ought practically to give 6400 kilogrammes, only yields 5760 kilogrammes, *i.e.* a loss of 10 per cent. in extract, or 16 per cent. on the weight of the liquor, which, after treatment, only titrates 3·6°, equal to a fall of 0·4°. As to the "nitrate" process, it is still worse, because the formation of free nitric acid eventually destroys a notable amount of tannin, owing to secondary reactions which take place in the concentration of the liquor in the evaporation plant, aided by the heat of that operation, to say nothing of the wear and tear by corrosion of the vessels in question owing to the presence of nitric acid. The authors tried to prevent this reaction by the addition of pure precipitated carbonate of lime, but the remedy was more aggravating than useful in the decoloration of the juices so treated. The contentions of the authors in regard to the decoloration of extracts are supported by the fact that numerous British and German tanners have used the crude extracts or extracts simply clarified by one of the mechanical processes already described for a long time, which ensure uniformity in the deliveries, and especially a higher percentage of tannin, and consequently a higher yield in leather. The decolorisation of the future does not lie in the use of chemical products, nor in more or less complicated processes; tanning is an industry already far too complex to allow of it; it requires, and will require, before and above all pure extracts, of a well-determined nature, with a high percentage of tannin, soluble in cold water, and finally of as constant and uniform a composition as possible. However, mention may be



made of Peyrussou's curious process of decolorisation, Brevet No. 318,523 (February 8, 1902), with certificate of addition No. 318,523,467, in which the patentee specifies that the process described in his principal patent rests especially on the action of the presence of tin, applied during the preparation of the tannin and tinctorial liquors and extracts, with the object of preventing the grey coloration of the latter. Thus in treating chestnut extract in a digester of any kind, in presence of tinfoil, it will be found that the wood remains white, whilst the same wood treated in the same way, but without tin, assumes a grey or even a brown tint. Finally, the method may be quoted of a recent patent, that of George Klenk, for a process of decolorising tannin liquors by the use of aluminium sulphate and sodium bisulphite, being as follows: Add to the hot liquors from the extractors, in a vat fitted with an agitator, a solution of sulphate of alumina (the quantity to use depending on the strength of the juice); after the mixture of these two liquors, add thereto bisulphite of soda  $38^{\circ}$  to  $40^{\circ}$  B. *q.s.*, stirring constantly. The following is the reaction:—



The average proportions to use are liquor at  $4^{\circ}$ , 5000 litres (1100 gallons), solid aluminium sulphate 4 kilogrammes (8·8 lb.), sodium bisulphite  $38^{\circ}$  to  $40^{\circ}$  B., 15 to 20 kilogrammes (33 to 44 lb.). This process is applicable to quebracho, mimosa, hemlock, sumac, pine, oak, chestnut, and others. The juice so treated is decolorised by aluminium hydrate in the nascent state, which agglutinates the resinous particles of the liquor, and falls with them to the bottom of the vat, precipitated in the same way as with albumen or blood. Moreover, the nascent sulphurous acid, which escapes during the decolorisation of the juice, has an intensive decolorising effect. After cooling to  $20^{\circ}$  to  $25^{\circ}$  C. decantation, concentration, etc., extracts are obtained, soluble in cold water, retaining an acid reaction, giving a pale yellow colour to leather, and differing slightly but sometimes not at all from oak tanned leather. Finally, the colour imparted to the leather by such extracts is permanent and is not liable to change under the ordinary action of the air. Notwithstanding the interesting aspects of these decolorisation processes, the authors maintain the opinion given above, and add that they all have drawbacks, both for the extract manufacturer and the tanner; the losses, whatever may be the process used, being from 2 to 3 per cent. of tannin to the detriment of the yield in extract, whilst the colour of the leather is in no way altered. The authors can, in fact, affirm that, having had occasion to

make many analyses of the tannin in different leathers, where extracts decolorised either by blood or by nitrate had been used all the leathers tanned by these extracts were darker than those yielded by other and well-clarified extracts, and that although the coloration of a 1 per cent. solution was less marked than a solution of clarified extract. Moreover, the tannery of the future will be that which utilises mixed processes of tanning, with extracts manufactured in a genuine manner and judiciously used; the opinion of Prof. Procter, the eminent English chemist, is decisive on this point. If it be desired to impart to manufactured extracts the necessary degree of solubility, recourse must be made to perfectly neutral materials, products already used by the tannery which are known to have no drawback; thus the authors, inspired by these conditions, have used borax to render chestnut extract soluble. The borax is used in tanneries as follows: "Borax may be used for many purposes in tanning and currying; its most important rôle is to soften the river water, to clean and preserve the skins, to avoid the loss of their gelatine, and thus to render the leather heavier and firmer; it prevents the pits from going bad and putrid, it is the most efficacious and harmless agent that can be found for preliminary rinsing and cleaning of skins before they are placed in the vat. With a kilogramme (2.2 lb.) 1000 litres (220 gallons) of the water generally used may be softened. Solution is effected in boiling water and it is run into the vat with energetic stirring." It was, therefore, after important and repeated tests, that the authors were led to adopt it as a solvent agent for extracts clarified according to the mechanical processes already described; the factory where the authors, *inter alia*, demonstrated this interesting question continues to use it on an output of 7000 kilogrammes per day, and they know, on the other hand, that the tanners who use it are perfectly satisfied therewith. At the minimum rate in which it is incorporated, it only enters into the composition of these extracts, in order to render the usual small percentage of insoluble, soluble in the cold. Added to the liquor, at a certain stage of the manufacture, it produces neither precipitate nor reaction of any kind.

*Manufacture of Chestnut Extracts of 25° B., 30° B. or Solid Extracts. Concentration or Evaporation of Chestnut Extracts.*—The treated juice or liquors, *i.e.* clarified according to the processes already described, pass directly from a liquor receiver to the evaporating vessels, represented in some factories by a double effect, in others and better still by a triple effect, the latter constituting, in the opinion of the authors, the most efficient plant and the one which ought preferably to be used. (The different systems used in tannin manufactures will be described later.) As stated, it must be taken that liquors of

3·8° yield 13 to 14 per cent. of extract of 25° to 26°, with 86 to 87 per cent. of water to evaporate; knowing on the other hand that the ton of wood treated yields on an average 1350 to 1650 litres of liquor (297 to 363 gallons) according to the method of working adopted, it is easy from such data to determine the evaporative capacity to impart to the vessels intended for the concentration of the liquor of a typical factory, the consumption of which is 60 tons of wood per twenty-four hours, which will be, moreover, described later. These vessels are fed in a regular manner, and it may be said that it is even possible to feed them automatically so as to do away with an attendant. A triple effect evaporating 20 litres of water per hour per square metre will thus yield the corresponding quantity of extract of 25°, say 2·7 kilogrammes. In No. 3 it may be taken that this hourly output will fall to 2·1 kilogrammes when making 30° extract. As to the steam consumption and always in the case of a triple effect, it is necessary to allow 7 kilogrammes for the evaporation of 20 litres of water per square metre per hour; finally, if a reheater be utilised prior to No. 1, the consumption may be appreciably reduced, and it may be said that the evaporation of that quantity of water apparently requires the amount of steam which corresponds to 1 kilogramme of coal or to 5 kilogrammes of spent chips. Although this yield appears satisfactory and suffices on normal working, the Kestner system, gives far superior results, as will be explained later. No. 3 is generally furnished with a syrup discharger or a special extract pump by which the extracts, when they have reached 25° or 30°, can be evacuated whilst the plant is at work and stored in tanks where they cool naturally before being sent out in casks. It may be said that these extracts, once placed in the vats, gain in quality by being left there to deposit for several days; the mud which they deposit being so much impurity removed. It is better to take these deposits and treat them together with the mud from the clarified juice; they can then be concentrated.

*Dry Extract.* — It is possible, by the rotary simple effect presently to be described, to push the concentration farther than 30° and to bring the extract to the dry condition; it is then necessary, for the production of 100 kilogrammes, to use 210 kilogrammes of 25° extract, or 170 kilogrammes of 30°, consuming 3 to 4 kilogrammes of steam. Its cost price is then fixed at about 25 francs (£1) the 100 kilogrammes (2 cwt.) for 45 per cent. tannin.

*Solution of Dry Extract.* — In order to dissolve dry extract, the water should not be cold but if perfect solution be required, heat to 60° C (140° F.) or higher. Crush the cakes to be dissolved and suspend the pieces in a willow basket in the upper part of the liquor. Let solution take place spontaneously until



the solid extract has disappeared. If the cake of extract be placed in the bottom of the liquid, it is impossible to dissolve it even when stirred continually with a rod. Only extracts soluble in the cold prepared as indicated by the authors are included in this method of working, extracts containing an appreciable amount of insolubles (more than 5 per cent.) require to be rendered soluble in an apparatus *ad hoc*, which will be described later when dealing with dry quebracho extracts (see p. 276).

*Factory Routine.*—It is indispensable for the good working of an extract factory that it should be subjected to efficient control day and night; a manufacturing schedule is therefore appended here with its control appendix by which the manufacture may be followed daily at any given moment. These documents also serve as the basis of strict book-keeping, hence errors become practically impossible without their being shown by the quarterly inventories which should be taken in a factory of this kind.

TABLE XXIII.—SCHEDULE ANNEXED TO TABLE XXII., No. , DATE , 1921. CONTROL

Average of the tables relating to each department and signed by the foreman or by the man in charge.	Observations.						Repairs.					
							Day			Night		
	1	Average pressure on the boiler . . . . .										
	2	„ strength of the liquors . . . . .										
	3	Number of triple effect boilings . . . . .										
	4	Average temperature of the water feeding the boilers . . . . .										
	5	„ „ „ „ feeding the autoclaves or vats . . . . .										
	6	„ „ „ „ from the refrigerators . . . . .										
	7	„ „ „ „ from the condensers . . . . .										
	8	„ „ „ „ cooled liquors . . . . .										
	9	„ „ „ „ hot gases . . . . .										
	10	State of the furnaces . . . . .										
	11	Draught in mm. at the fan or chimney . . . . .										
	12	Average vacuum in the three vessels . . . . .										
	13	„ temperature of the three vessels . . . . .					1	2	3	1	2	3
	14	Weight of 25° or 30° extract made vat No. . . . .										
	15	Tannin per cent. of average liquor . . . . .										
	A	Per cent. of tannin in 25° extract . . . . .										
	B	„ „ „ 30° „ . . . . .										
	C	„ „ „ gallo-sumac . . . . .										
	D	„ „ „ quebracho . . . . .										
	E	„ „ „ special 25° . . . . .										
	F	„ „ „ oak 25° . . . . .										
		Tannin per cent. of wood treated, Lot No. . . . .										
		Moisture „ „ „ „ . . . . .										
							Chief works chemist.					

*Evaporation by Direct Steam.*—Following the example given by M. P. Kienlen in his remarkable “Examination of the

different Systems of Evaporating Lyes" in his "Soda and Paper Industries" (*Mon. Scientifique*, 1898), the authors propose their turn to pass in review the different evaporation plant used in the important tannin industry for the concentration of the juice or tannin liquors, from 4° to 25° or 30° B., the hydrostatic strength at which they are valued commercially.

*Concentration by Indirect Heat: Evaporating Pan with Chenailier's Coil.*—As in this industry, the use of direct steam for the concentration of the juice—whether in a pan fitted with steam coil or with a Chenailier's coil—oxidises and destroys the tannin by the high temperature of the steam (150° C. or 27° F. with a pressure of 5 kilogrammes) passing through this style of apparatus in the open air, and as such plant is of cumbersome dimensions, and at the same time consumes an excessive amount of steam, it will be adverted to only as a matter of history, mention however being made of Chenailier's steam evaporating plant (Fig. 102), which might be used if desired for the evaporation of liquor intended for crude chestnut extracts (e.g. gallic for dyeing), or logwood or other dry tinctorial extracts. It need only be added that a Chenailier's apparatus requires 1 kilogramme of steam per hour per square metre, when simple effect expends 1.1 kilogrammes, a double effect 0.72 kilogramme, and a triple effect 0.360 kilogramme to evaporate the same amount of water.

*Plant for Evaporation under Reduced Pressure (Vacuum Pans).*—In the sugar industry was employed the first plant based on the principle of lowering the boiling-point of a liquid or bringing that liquid to the state of vapour under a pressure less than that of the atmosphere. Howard, an engineer, was the first to introduce into British sugar refineries, in 1813, the first appliance of this nature, using, moreover, for the production of the vacuum a barometric condenser with countercurrent and dry air pump. Later Derosne designed similar plant, but with surface condensers in which the diluted juice acted as the refrigerating agent. Finally, the principle of the multiple evaporation system was applied in America by Rillieux in 1830 then in Europe about 1850. During this time numerous improvements were sought to bear thereupon by Tischbein, Robert, Degrand, Walkhoff, Cail, and Derosne, but the merit of their development in the French sugar industry belongs to Cail & Co. and more recently to the Fives-Lille Construction Co., and mention may also be made of the firm of Bonnet-Spazin, who have specialised in the construction of plant intended for use in the tannin industry since 1877. Such plant is constructed on the principle of utilising the latent heat which is disengaged from the liquid being evaporated—which heat is lost in those pans that are heated indirectly or in the open air—to heat fresh

quantities of liquid to be evaporated in one or more vessels communicating consecutively with each other. The arrangements for simple, double and triple effect used in the tannin industries will be described and the essentials of maximum utilisation, as much from the point of view of the amount of water evaporated per hour as from that of the economy in steam which can be realised, the relation of these to one another being most important to ensure a high capacity.

*Simple Effect.*—This, the simplest type, comprises a closed pan (which the French call a *casse*) in which the pressure is lowered by the rarefaction of the air at the exit of the steam from the pan. The heating steam (the escape steam from the engines or coming directly from the steam boilers) is injected

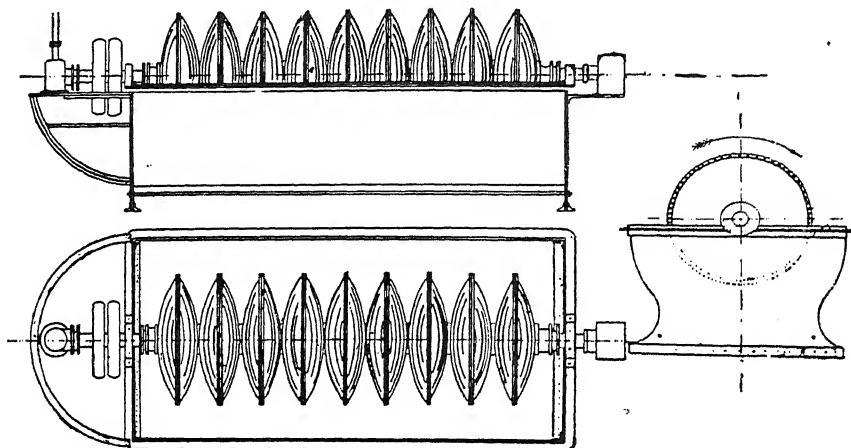


FIG. 102.—Chénaillet's evaporator.

into the steam chamber of the pan. The calandria is provided with two horizontal tubular bronze plates pierced with holes, in which there are fixed *par dudgeonnage* the tubes of a tubular bundle, thus forming a large heating surface. There is formed in this way around this tubular bundle a heating chamber occupied by steam, the juice to be evaporated being inside the tubes. The authors remark that it would be more satisfactory to cause the steam to pass inside the tubes, after the style of a tubular reheater, and to allow the juice undergoing evaporation to circulate all around the exterior; however, practice has shown that the converse is the case, taking into account the facility for cleaning the tubes which, eventually becoming encrusted, require cleaning by brushes, so as to preserve the maximum evaporating capacity of the apparatus. The steam penetrating into the heating chamber condenses, imparting its latent heat

to the juice to be evaporated, the latter boils under the reduced pressure, and thus yields a fresh amount of steam. The water from the condensation of the steam in the heating chamber is run off through a blow-off pipe, usually by an automatic blow off which prevents the passage of steam. This water is used to feed the boilers. The steam from the boiling juice is condensed in a surface condenser, placed in front of the air pump, at the exit from the pan, yielding a corresponding quantity of hot water, which is used for macerating the wood. With a barometric or with an injection condenser, the steam mixed with the condensation water passes down the drain and is a distinct loss, therefore the authors recommend the exclusive use of a surface condenser in all cases, simple, double and triple effect, because they hold, as shown previously (Chap. I.), that in a tannin factory the maximum yield and highest percentage of tannin are obtained by the use of water as pure as possible for the maceration of the wood. The condensed waters from the evaporating vessels are therefore obviously indicated, and, in default of a system of surface condensation to collect them, a special pump is required called the condensed water pump, in both double and triple-effect working.

*Installing a Simple Effect.*—This apparatus, now slightly modified, was described by Othon Petit (*Des Emplois chimiques du Bois dans les Arts et l'Industrie*, 1888). A more improved form of this plant is, therefore, shown here (Fig. 103), combined with a juice reheater, R, and a wet air pump. This arrangement is particularly suitable for tanneries in which the object is to concentrate bark, diffusion juices, or juices from the maceration of wood, or weak juices regenerated from the train of vats, after treatment and clarification, manufacturing in this way easily and economically thick juice of 12° to 15° B, which serves to enrich those at work. Here are the details of this plant which comprise: (1) A vessel, A, of 20 square metres of heating surface, capable of evaporating 1000 litres (220 gallons) of water per hour. This apparatus is made entirely of copper and bronze in those parts which come into direct contact with the juice and consists of a tubular calandria 1 metre in diameter, height between the tubular plates 0.77 metre, thickness 5 mm., in the bottom 6 mm.; an upper calandria, diameter 1 metre, height 1 metre, thickness 5 mm., in the bottom 6 mm.; a safety vessel, V, 600 by 600 mm., thickness 3 mm., in bottom 4 mm.; two tubular bronze plates, 16 mm. thick; a tubular bundle comprising 162 tubes in electro-copper of 50 mm. external diameter, thickness 2 mm., a copper steam inlet connecting pipe on the tubular bundle, a copper connecting pipe for the passage of the steam to the safety vessel, a connecting pipe and a pipe of 35 mm. diameter for the return of the entrained liquor; iron joint



bands; cast-iron supports. It is also fitted with taps and the following accessories: one bronze tap 40 mm. for liquor inlet. One bronze three-way tap 10 mm. for discharging the extract and the wash water. One connecting pipe all bronze for blowing off the condensed water. Gauge glass vacuum indicator. Air tap. Anti-froth tap. Wash water tap. Test glass for sampling. Manhole doors in bronze 400 mm. diameter. Round peepholes 100 mm. Tap for evacuation of uncondensable gases. The complete plant weighs 1625 kilogrammes ( $1\frac{5}{8}$  metric tons

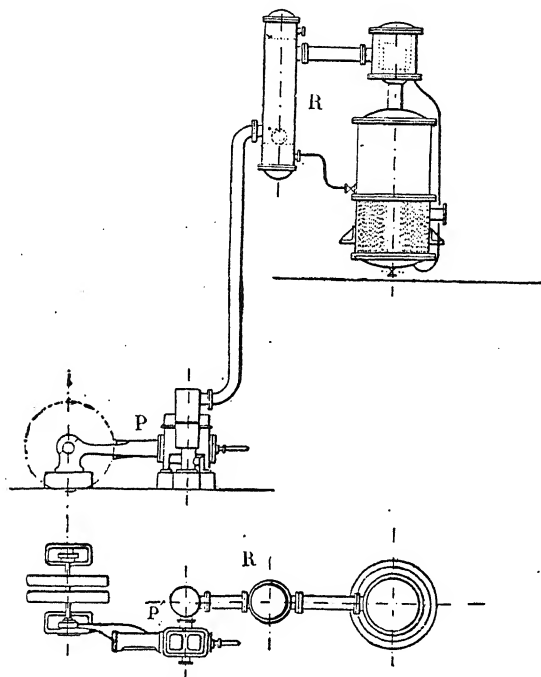


FIG. 103.—Simple effect evaporation plant with reheater and its pump.

or about 32 cwt.). The air pump, P, serving this triple effect, with its condenser, C, entirely of copper and bronze in the parts connected with the steam, capable of condensing 100 kilogrammes of steam per hour, is driven either by a belt, or by a direct motor.

*Juice Reheater.*—As already remarked, and, moreover, shown in Fig. 104, the juice to be concentrated traverses the tubular bundle of a copper reheater, consisting of a cylindrical calandria of 2 metres by 400 mm., of two tubular bronze plates, one upper manhole, one lower manhole. The tubular bundle consists of thirty-seven copper tubes of 40 × 45 mm., representing 8 square metres of heating surface. A juice inlet connection

pipe for the distribution chamber and a discharge pipe complete this apparatus, into which the juice runs, between 15° to 20° C. (59° to 68° F.), issuing at 50° to 55° C., a temperature at which it is brought by the steam from the simple effect circulating round the tubular bundle of the reheater before it passes to the air pump and the condenser. This simple apparatus realises a notable economy in steam, which may be estimated at 9.4, 5.3 per cent. in triple, double, or simple effect.

*Rotary Simple Effect.*—The rotary type of simple effect, designed by Bonnet-Spazin & Co., of Lyons, in which the tubular bundle revolves, may be described here. This system, where the juice to be concentrated circulates around steam pipes, is especially suited for the manufacture of chestnut, quebracho, logwood, or other dry extracts. It has certain advantages over Chenailier's system previously described. It consists (Fig. 104) essentially of a horizontal copper calandria, fitted with a double bottom, and surmounted by a safety vessel, inside of which is a froth breaker, two bottoms or linings of copper plates pierced with a central hole closing its two extremities.

Inside there is a tubular bundle, consisting of copper pipes 2 mm. thick, 40 by 45 cm., the extremities of which are dudgeoned into the orifices of two tubular bronze plates of 18 to 20 mm. thick. A hollow central shaft traverses the whole system from one end to the other, and receives the steam, which it distributes into all the pipes, which enters the tubular plates and the linings of the tubular bundle, where the condensed steam is blown off through the double bottom to be afterwards evacuated. The tubular bundle revolves in the glands of two stuffing boxes, which are fixed in the centre of the dome part of the calandria; the extremity of the hollow shaft again rests on two bearings with stuffing boxes provided with glands, the one serving as a steam inlet, the other as an outlet for the condensed water evacuated by the rotation of the tubular bundle and the pressure of the steam, which cause it to pass into the double jacket, whence it escapes to be utilised in feeding the boilers.

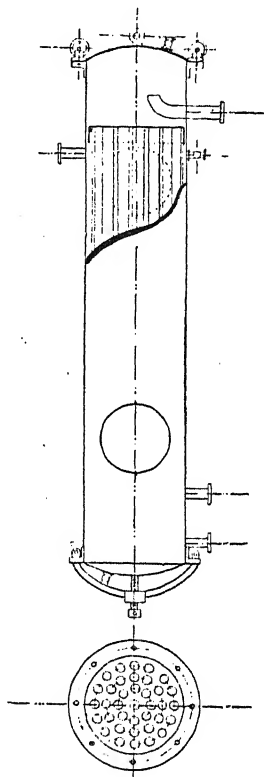


FIG. 104.—Tannic liquor reheater.

*Double Effect.*—This type consists of two closed vertical pans communicating with each other, in which the pressure is lowered by rarefaction of the air at the extremity of the system. The heating steam, as in the simple effect, entering the heating chamber of the first pan, condenses, giving up its latent heat to the liquid to be evaporated, the latter then boils under slightly reduced pressure, thus yielding a fresh quantity of steam. This steam is utilised to heat the tubular bundle of No. 2 vessel which is in communication with No. 1; thus the liquid in No. 1 is caused to boil under a further reduced pressure, produced by the rarefaction of the air in the second vessel, by means of a special pump. Fresh quantities of water condense in the heating chamber of No. 2; the steam arising from the boiling of the liquor in this vessel is condensed in a surface or injection condenser placed in front of the air pump at the exit of No. 2, after

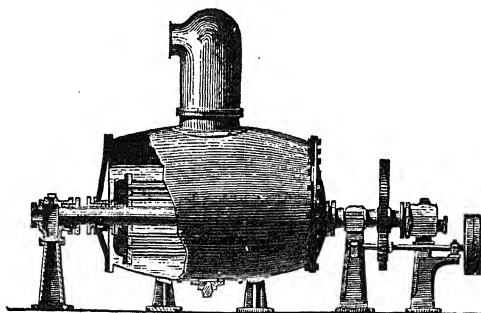


FIG. 105.—Horizontal rotary simple effect concentration plant.

having traversed the tubular bundle of a juice reheater. The heating chamber of No. 2 may be connected with a condensed water pump (the water from which is used for the maceration of the wood), a centrifugal pump, for example, which pumps it to the condensed water reservoir feeding the vats or autoclaves. Fig. 106 shows a double effect with 90 square metres of heating surface, capable of evaporating 2250 litres (475 gallons) of water per hour with barometric condenser, condensed water pump and dry air pump worked tandem by direct motor. The safety vessel shown is of the system with multiple perforated baffles; it gives very good results, as a froth breaker, in the evaporation of oak liquors, which froth considerably. It may be remarked, that an increase in the number of vessels does not result, as one might believe, in an increase in the production of the system, but simply in a decrease in the steam expended, as also in the amount of water used for condensation. Moreover, the number of vessels appropriate for the work does not

depend so much on certain peculiar cases, as in alkali manufacture, or in sugar manufacture; the authors' experience in the matter enables them to assert that for a tannin factory to work economically, that is to say, to use exhausted wooden chips solely as fuel (the use of coal would, moreover, point to

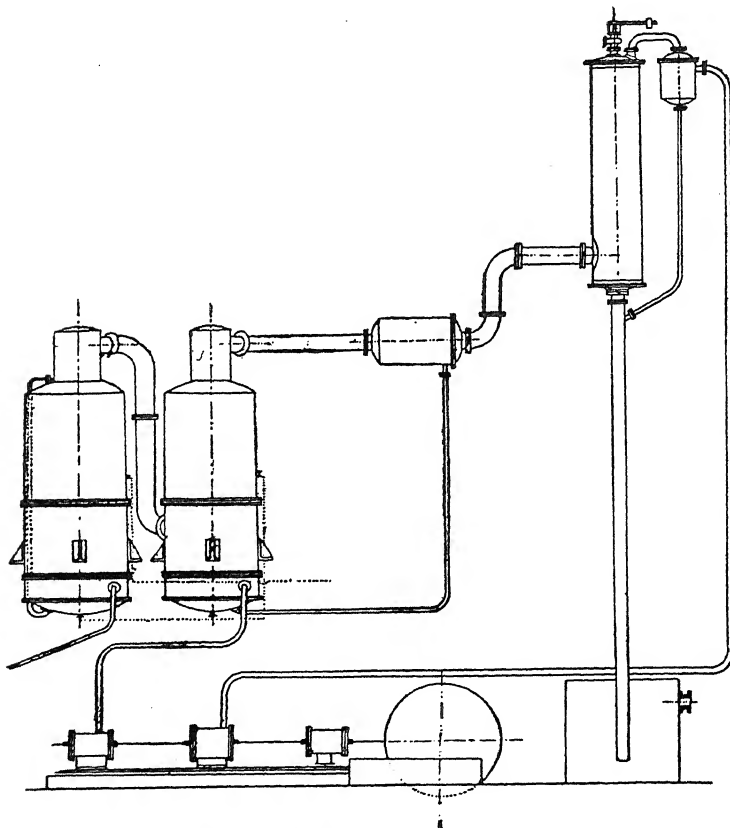


FIG. 106.—“Double effect” with its barometric condenser and its two pumps driven in tandem by direct motor.

abnormal working, bad arrangement of plant and apparatus, or obsolete processes), it is best to use an improved triple effect.

*Theory of the Triple Effect.*—Suppose the heating steam in No. 1 be at  $100^{\circ}$  C. and the liquid arriving at its boiling point say,  $84^{\circ}$  (see Fig. 107). The heating steam is condensed at  $84^{\circ}$  C. and gives up a quantity of latent heat = to  $496.3 + 40.20 + 16 = 552.50$  calories per kilogramme of steam. The liquor in No. 1 is vaporised at the temperature of  $84^{\circ}$  C. To vaporise a kilogramme

of water at that temperature the amount of heat required is  $507.12 + 39.04 = 546.16$ , hence 1 kilogramme of condensed steam in No. 1 vessel can vaporise  $\frac{552.50}{546.16} = 1.015$  kilogrammes of liquid in that vessel. No. 1 steam at  $84^{\circ}$  condenses in No. 2 at  $73^{\circ}$  C. Each kilogramme of steam, converted into water at  $73^{\circ}$  C., gives up  $546.16 + 11 = 557.16$  calories. The liquor entering No. 2 at a temperature of  $84^{\circ}$  C. is converted into steam at  $73^{\circ}$  C.; it requires for that an amount of heat equal to  $546.16 - 11 = 535.16$  calories. Hence 1 kilogramme of steam condensed in No. 2 vaporises  $\frac{557}{535} = 1.039$  kilogrammes of liquid in that vessel. No. 2 steam produced at  $73^{\circ}$  C. is condensed in No. 3 into water

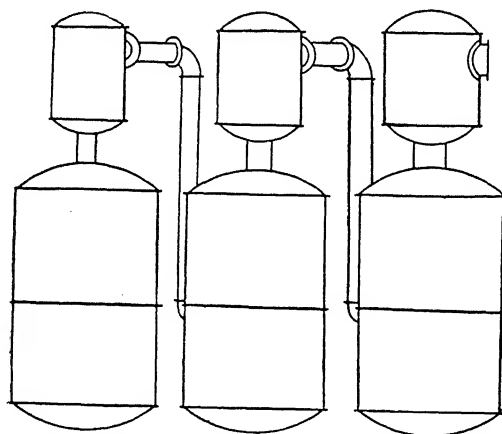


FIG. 107.—No. 1.  
Vacuum 35-40 cm.

No. 2.  
50-53 cm.

No. 3.  
60-67 cm.

at  $54^{\circ}$  C. One kilogramme of steam at  $73^{\circ}$  C., converted into water at  $54^{\circ}$  C., gives up a heat of  $550.6 + 19 = 569.6$  calories. The liquor entering No. 3 is at  $73^{\circ}$  C. and it is reduced to steam at  $54^{\circ}$  C. It requires for that per kilogramme a heat of  $550.6 - 19 = 531.6$  calories. Hence a kilogramme of steam condensed in No. 3 vaporises  $\frac{569.6}{531.6} = 1.071$  kilogrammes of water therein.

To sum up, 1 kilogramme of steam entering No. 1 at  $100^{\circ}$  C. produces a kilogramme of condensed water at  $84^{\circ}$  C.; 1.015 kilogrammes of steam in No. 1, which is converted into 1.015 kilogrammes of condensed water at  $73^{\circ}$  C., will produce  $1.015 \times 1.030 = 1.050$  kilogrammes of steam in No. 2, which condenses into 1.050 kilogrammes at  $54^{\circ}$  C., which produce  $1.050 \times 1.070 = 1.125$  kilogrammes of steam in No. 3, which goes to the con-

denser. Hence, finally, 1 kilogramme of steam at 100° C. induces the evaporation of 1.015 of water in No. 1, of 1.050 in No. 2, of 1.125 in No. 3—a total of 3.190.

TABLE XXIII.—SHOWING BALANCE OF THE ACCOUNT OF STEAM EXPENDITURE AND RECOVERY IN THE WORKING OF TRIPLE EFFECT PLANT IN THE CONCENTRATION OF TANNIN EXTRACTS.

There were in the beginning:—

	Calories.
1 kilogramme of steam at 100° C., containing . . . . .	636
3.190 kilogrammes of liquor at 84° C., containing . . . . .	336
Total . . . . .	<u>972</u>

There is recovered at the end of the operation:—

	Calories.
1 kilogramme of water at 84° C., possessing . . . . .	84
1·015 kilogrammes of water at 73° C., possessing . . . . .	74
1·050        "                  "                  " 54° C.,        "        . . . . .	56
1·125        "                  of steam at 54° C.,        "        . . . . .	698
	<hr/> 912

*Weight of Water Evaporated per Vessel by a Triple Effect Plant.*—The evaporative capacity of a vessel is proportional to the heating surfaces and to the difference in temperature between the steam and the liquid. It depends on the state of the tubes and of the density of the liquid in virtue of its resistance to the motion of circulation. Let the two last elements be neglected. No. 1, 1 square metre; No. 2, 1 square metre; No. 3, 1 square metre. Take the temperature of the heating steam as  $100^{\circ}$  C., the vacuum as 65 cm. in No. 3 giving  $54^{\circ}$  C. Total difference,  $100 - 54 = 46$ . Dividing this difference into three, say 15.3, the apparatus ought to be regulated to have a temperature of

$$\begin{array}{rcl} 100 - 15.3 = 84.67 \text{ in No. 1, } 76 - 43 = 33 \text{ cm. vacuum} \\ 84.67 - 15.33 = 69.34 \text{ in No. 2, } 76 - 22 = 54 \text{ " " } \\ 69.34 - 15.34 = 54 \text{ in No. 3, } 65 \text{ " " } \end{array}$$

and the three vessels will do an equal amount of work.

*Triple Effect.*—As already stated, the triple effect system of evaporation under reduced pressure is much the best system for tannin factories or dyewood extract factories. It ensures constant and economical working by its comparatively great evaporating capacity, coupled with a minimum steam consumption as demonstrated above by calculation. Each system varies somewhat with the construction of the plant, following the advice of the chemical engineers of the industry in regard to improvements. Several types will now be studied.

*Type I.*—Triple effect of 150 square metres of heating surface (this example is taken as representing the average build of

this type) combined simply with an injection condenser and a pump or wet-air vacuum. Evaporative capacity 3000 litres (660 gallons) per hour, or 20 litres (4.4 gallons) per hour per square metre. In this case it is plain that the steam economy depends upon the number of vessels. The condensed water from Nos. 2 and 3 going direct to the condenser mix with the injection water. Consequently it is totally ejected by the condensed water pipe. This arrangement (Fig. 108), which is the simplest ought not to be used unless unavoidable; it should be completed by a condensed water pump as will be shown in Type III.

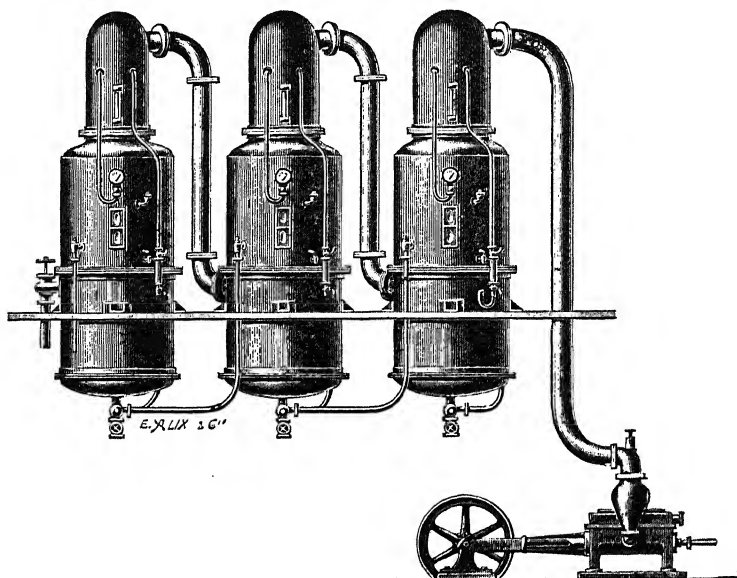


FIG. 108.—Triple effect evaporation plant.

*Type II.*—Triple effect of 150 square metres (three equal vessels of 50 square metres) combined (1) with a countercurrent barometric condenser; (2) with a condensed water pump; (3) with a dry air pump, tandem system by direct motor. The steam from Nos. 1 and 2, condensed in the heating chambers of Nos. 2 and 3, are aspirated and collected by a special condensed water pump, which maintains the vacuum in the ebullition or evaporation calandria of Nos. 1 and 2, by means of suction valves. This condensed water pump, 150 mm. by 320 mm., with four valves, two for suction and two for propulsion, all made of bronze, do not propel further than a metre, so a *capot*, about the level of the propulsion pipes, receives the condensed

water from Nos. 2 and 3 vessels, to be afterwards propelled by a special (bronze) centrifugal pump to the feed condenser, to be utilised in the maceration of the wood. The copper condenser is of a new type, countercurrent with perforated baffles 650 mm.  $\times$  3 m., water separator and injection valve. It is completed by a barometric column 250 mm. in diameter and 12 metres in length. The air pump with direct horizontal

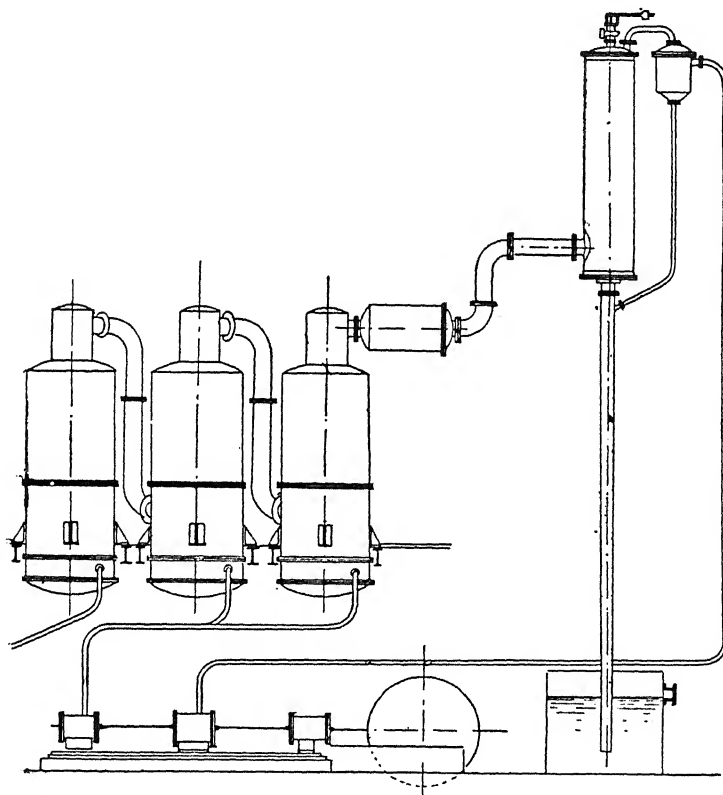


FIG. 109.—“Triple effect” connected with its barometric condenser, its dry air pump and condensed water pump in tandem (Bonnet-Spazin).

motor, bayonet system, 250 mm.  $\times$  320 mm., air cylinder 300 mm  $\times$  320 mm. Fig. 109 represents the plant on the scale of 1: 50, as arranged in certain factories where it yields good results. Although the fixing of the barometric condenser requires a minimum height of 11 metres it may be said that it works normally in all its applications.

*Type III.*—Triple effect of 150 metres combined with (1) a wet-air pump and injection condenser, which works, in parallel,



a condensed water (from Nos. 2 and 3) pump; (2) an automatic feed appliance (Koerting's) placed to the left of Fig. 110, propelling directly to the steam boiler the blow-off water from No. 1. Fig. 110 shows the arrangement which is, in fact, the average modern one. As will be seen, each vessel is fitted with a Heckmann's safety vessel, which suppresses the old arrangement, the utility of which has been justly disputed. To complete this plant, it is necessary to add a juice reheater such as shown in Fig. 104, the economy in steam realised by this having already been referred to.

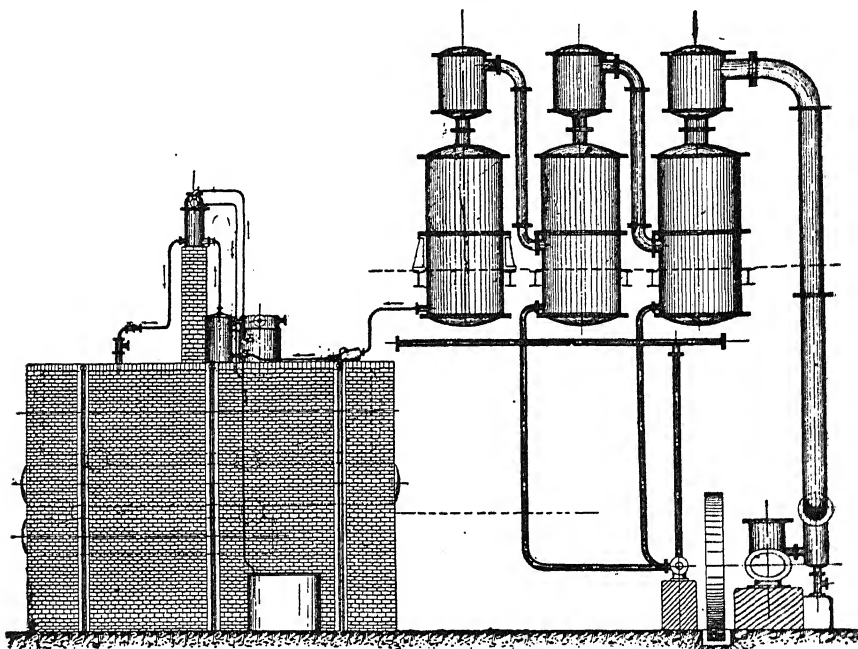


FIG. 110.—“Triple effect” combined with moist air and condensed water pumps, the water blown off from No. 1 being propelled to the boilers by Koerting's automatic feed.

*Type IV.*—Finally, and it is this type which the authors would like to see adopted more frequently instead and in place of the injection or barometrical condenser, a surface condenser, capable of condensing all the tannin vapours. For it must not be forgotten, that the vital question in tannin manufacture is the purity of the maceration water, besides which, the calories recuperated correspond to an appreciable economy in steam, which results in regular, constant, and, so to speak, automatic working. Thus, in adopting surface condensation, Derosne or tubular type, in which the tannin vapours from No. 3 circulate

and completely condense, and allow the incondensable gases only to pass to the dry air suction pump, a notable improvement will be realised in present plant. Practical data enable the authors to assert that, in the case of a triple effect of 150 square metres, a tubular condenser of 65 square metres, in which circulates as refrigerating agent, not the juice as in the Derosne system, but the water coming in abundance from the liquor coolers, will suffice. Moreover, this arrangement is only complementary to the juice reheater placed originally at the steam exit from No. 3. This last installation is completed by the addition of a pump for the condensed waters from Nos. 2 and 3, which, collected with those from the surface condenser, are propelled to the maceration plant passing through the feed reservoir of the vats or autoclaves.

*Air Pumps. Condensed Water Pumps. Wet Air Pumps.*—Types are very numerous, and it would take too long to enumerate them here, but pumps offering the greatest guarantee in simplicity and in the strength of their parts, with the least number of valves possible, two for suction, two for propulsion, their speed not exceeding fifty revolutions a minute, are always to be recommended. Finally, the pump should have a direct steam motor, the escape steam from which can be used to heat No. 1 vessel. This same pump will work, either parallel or tandem, another pump, called the condensed water pump, all of bronze, and which serves, in the case of a double effect, to draw the condensed tannin water from No. 2, and in the case of a triple effect, that from No. 2 and No. 3 vessels. Figs. 109 and 110 have already shown the position and the shape of these pumps. Two of these pumps are shown here: Fig. 111 represents an air pump with direct motor, and Fig. a 112 vertical twin made by Kobatel, Buffaud & Co. of Lyons.

*Dry Air Pump.*—This type of pump, which is used in working with a barometric or surface condenser, is generally coupled tandem with the preceding. It also is always driven by direct motor; its air cylinder has drawer distribution and arrangement for the suppression of injurious spaces. There is an advantage in constructing this pump entirely in bronze, in the same way as the condensed water pumps; as to the wet air pump, the interior organs—rod and piston, cylinder jacket, valve seats—should or can be all in bronze.

*Triple Effect Plant. Starting and Working of Type III. Testing Tightness.*—It is necessary about every fortnight, and also every time that a defect is noticed in the working of the plant, to perform a tightness test, to make sure that no air is entering and that all the joints are secure. The test is carried out as follows. Close all the taps which place the vessels in communication with the open air: the large steam escape taps,

the live steam taps, the discharge taps of each vessel, the "butter" tap.<sup>1</sup> Make full joints on the blow-off pipes of No. 2 and No. 3 and on the collar which connects with the double condensed water pump. Close the water inlet tap to the condenser, fill the cylinder and the upper evacuation chamber of the air pump with water. Open the three taps for blowing off uncondensable gases. Close the liquor inlet taps of No 1 and leave the others open; that done, start the air pump to work, so as to produce a vacuum in the three vessels; increase this vacuum as much as possible. If the piston is in good working order, as well as the glands of the stuffing boxes, 65 to 67 cm. of vacuum

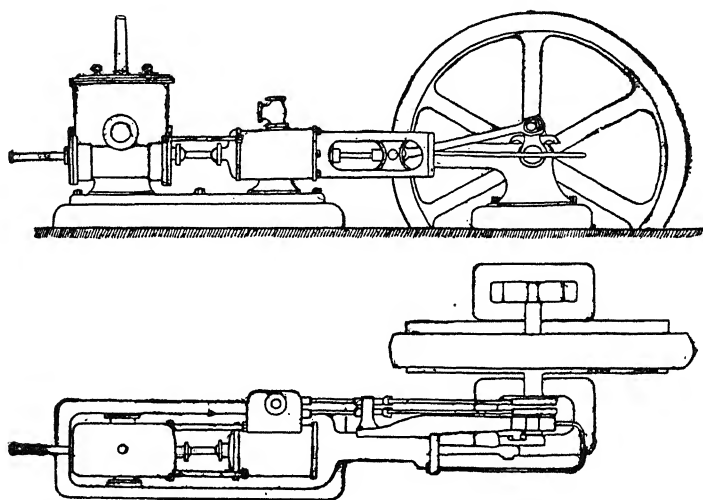


FIG. 111.—Moist air pump with its steam motor.

may be easily obtained. The pump is then stopped. If the vacuum falls very slowly, it is a proof that all is tight; if the vacuum falls quickly, it is a sign of a leak in one of the vessels or in the piping. In this case it is necessary to find the leakage; the whistling which occurs when air enters anywhere is a convenient indicator to find it. One can, moreover, ascertain from which vessel the leak takes place, by closing first the liquor tap and that for the evacuation of the uncondensable gases from No. 2, thereby isolating No 1. If the fall of the vacuum stops in No. 1 vessel, that is a proof that the leak does not occur in that vessel; if, on the other hand, the fall is more rapid then the leak is to be found in that vessel. No. 2 vessel is isolated in the same way, closing the liquor tap and the tap for

<sup>1</sup>The *robinet à beurre* supplies oil to float on the surface of the liquid, being evaporated so as to act as a froth preventive.—D.G.

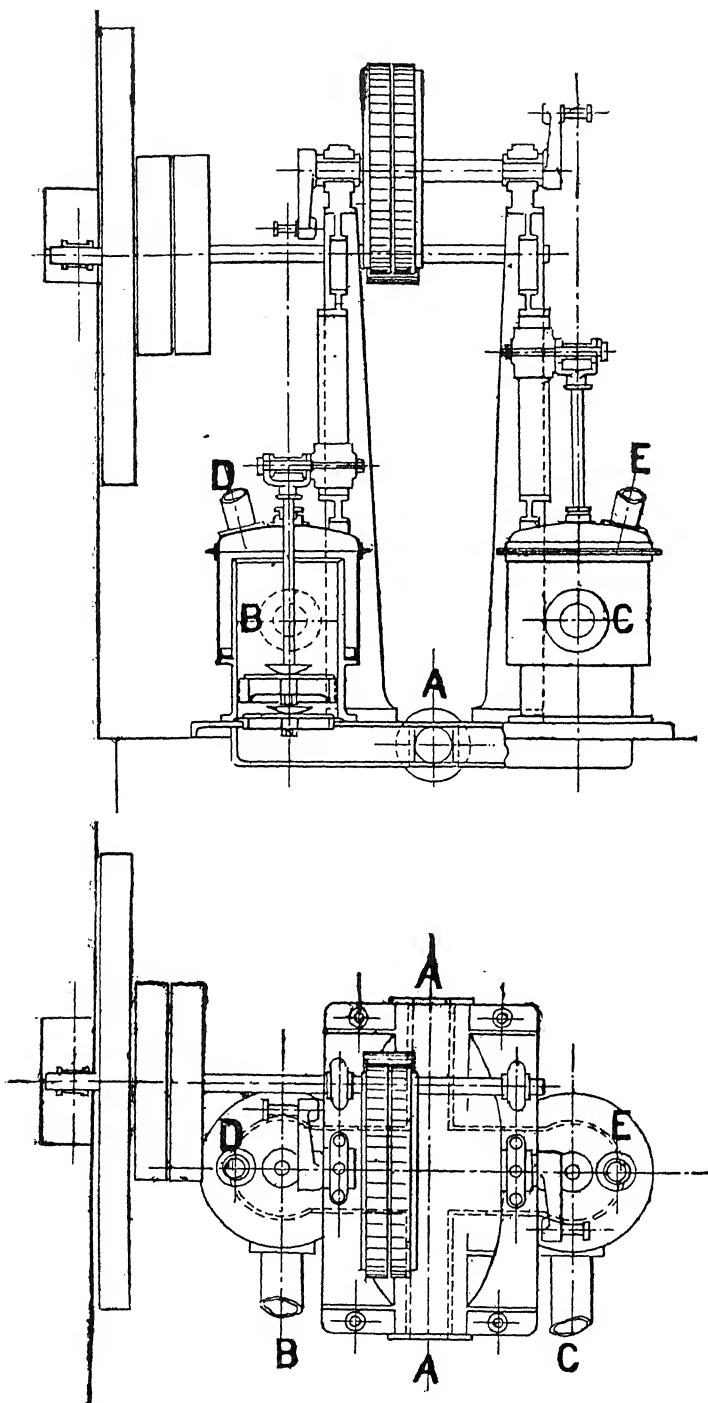


FIG. 112.—Twin wet air belt driven pump. AA, aspiration pipes for water and gases; BB, discharge pipes for condensed water; DE, uncondensable gas pipes.

the evacuation of the uncondensable gases of No. 3. It must be emphasised that any entrance of air leads to the inefficient working of the triple effect, and that it is, therefore, necessary to correct it at once.

*Starting.*—When tightness is secured a start is made as follows. Care is taken to remake the joints on the blow-off piping of No. 2 and No. 3 on the double condensed water pump. Close the liquor inlet taps of the three vessels; open, to its normal point, the water inlet tap to the condenser. Start the air pump; a vacuum is made in the three vessels, and when it reaches 30 cm. in No. 1, and 64 in No. 3, open the liquor feed tap in that vessel. Let the juice run in to the level of the tubular plate. Close the feed valve. At the same time open slightly the escape valve of the engines, so as to turn the escaped steam on to No. 1; the liquor in No. 1 soon commences to boil. Then open the feed valve of No. 2 to admit the liquor into that vessel. At the same time, again, open the tap of No. 1, to maintain its level. Let the liquor run into No. 2, until the boiling froth appears at the glass, and then open, finally, the feed tap of No. 3, to admit the liquor. As in No. 2, the liquor is allowed to reach only to the top of the tubular plate. During the whole time of this period of feeding continue to heat No. 1, so as to maintain therein the vacuum at 35 or 40 cm.; to do that it is necessary to increase gradually the opening of the escape valve of the engines, or to apply direct steam. Continue likewise to increase the quantity of liquor in No. 1 and in No. 2, but taking care not to allow the level of the liquid to rise too high. Starting from the moment when No. 3 is fed, the ordinary working of the triple effect commences. The following rules must then be observed:—

*Rules to Follow in Ordinary Working of Triple Effect.*—The two essential precautions in the working of the triple effect lie in the heating of No. 1 and in maintaining the level of the liquid in the three vessels. No. 1 must be heated, more or less, so that the vacuum is maintained uniformly at 35 or 40 cm. In the other vessels, the vacuum establishes itself, and working is normal when there is a vacuum of 50 to 55 cm. in No. 2 and 65 cm. in No. 3. The levels must be kept at such a height that there is no entrainment in any of the vessels, *i.e.* so that the froth does not rise too high and so be entrained into the safety vessel. Daylight must always be seen between the front peep-glass of the vessel and that above the bottom behind. If boiling be too violent in one of the vessels, the feed should be reduced, so as to lower the level. If the liquor be at any moment observed to prime, which may be seen by aid of the peep-glass on the safety vessel, the air tap is opened a little so as to lower the vacuum slightly in that vessel, the effect of

which is to stop the boiling at once. At the same time the feed of that vessel is reduced. Care must be taken in reducing the feed of a vessel to reduce that of those which precede it in the same ratio, otherwise the level of the latter will ascend. The vacuum in No. 3 should be 65 cm. This point is arrived at by appropriately adjusting the water inlet tap of the condenser. It is evident that the amount of water injected should be capable of condensing the steam from No. 3. The temperature of the mixture of hot water, which is ejected by the pump, ought to be  $30^{\circ}$  to  $35^{\circ}$  C. at the maximum. It is evident that in winter less water for condensation will be necessary than in summer. If, in spite of regulating appropriately the volume of water injected, the vacuum does not stand at 65 cm., the condition of the segments of the piston of the air pump of the stuffing boxes with glands and the rubber valves must be ascertained or it may be necessary to make a tightness test. Care must be taken to see from time to time that the blow-off cocks of each vessel are in good working order. The concentration of the liquor is greater in proportion as the evaporation progresses in No. 3.

*Sampling.*—Samples are taken by aid of a special appliance adapted to each water-level as follows. Close the lower and open the upper tap of the reservoirs. When the reservoir is filled with liquor, close the upper tap, which brings the interior of the reservoir in communication with the atmosphere by the small air-hole; the juice then flows into the sample vessel, in which it is tested by dipping a hydrometer into it. To aspirate the juice, open the two taps and close the top one, when air bells are seen to rise up the water-level.

*Discharging the Extract.*—When the liquor in No. 3 is of the desired strength, it must be evacuated, which is done by aid of the juice pump or the "syrup discharger". Close the three liquor inlet taps on the three vessels and turn off the steam heating No. 1, allowing the vacuum to fall in No. 3 to aid the discharge. The piston rod of the extract pump is locked, and the discharge tap of No. 3 is opened or the syrup discharger is brought into gear. When the vessel is empty the discharge valve is closed, the pump unlocked and No. 3 vessel refilled through No. 2, and No. 2 through No. 1, thus resuming normal working. Care must be taken that the bulk of the mass boiled in No. 3 does not rise 10 cm. (4 inches) above the tubular plate, so as to avoid loss of juice by the condensed water pumps and the dial tap.

*Stopping the Triple Effect Plant.*—Preliminary to stopping, the feed taps of each vessel must first be closed. The steam heating No. 1 must be discontinued by turning the escape valve as to blow off into the open air, and the air pump is stopped.

*Restarting.*—Set the air pump to work. Open the steam inlet tap so as to turn heating steam on to No. 1, and when the boiling has resumed its usual course the juice feed is turned on.

*Cleaning.*—Care must be taken in order to maintain a regular output, to clean the tubular bundle and wash the vessels at least once a month. It must be realised that encrustations on the inside of the tubes considerably diminish the output of the apparatus, and that it is very desirable to remove these encrustations, as often as practicable, to prevent them hardening. To clean No. 1 brushing and washing with hot water often suffices, likewise for No. 2. In No. 3 the encrustations become very hard, and it is then necessary to use a special apparatus, called the turbine brush. To facilitate the work of cleaning, water may be boiled in the vessels; to do this it suffices to fill them with water up to the level of the plates and turn on live steam into the heating chambers. This softens the hard encrustations and aids their removal by brush and scraper. The wash waters are evacuated through the wash collector, which discharges them down the drain.

*Kestner's Evaporator.*—The evaporation plant in common use has now been reviewed. A new system, based on a principle but little known, by which a much greater output and an absolutely rational working of the plant is realised, now remains to be described. These evaporators are of comparatively recent introduction, but their applications multiply from day to day in all industries where evaporation has to be effected. The evaporators referred to are those of the Kestner Evaporator & Engineering Co., Ltd. This plant is constructed so as to be heated by live steam from the boilers or escape steam from the engines; they are simple, double, triple or multiple effect; concentration being effected in tubular bundles 7 metres in length. The liquor, distributed in the lower part of the plant by a special arrangement, distributes itself equally through all the tubes of the bundle, conditions which realise a great advantage in obviating damage to products sensitive to heat; as is the case with wood extracts, from the point of view of the liquid in circulation, the differences are remarkable compared with other systems; thus for two sets of plant doing the same work an ordinary quadruple effect of the type previously described contains 15,000 litres in process of concentration, whilst Kestner's plant contains only 500! This difference clearly indicates that a new principle is applied in this evaporator; it is the phenomenon termed "grimpage" or "climbing" which causes the liquid to rise in tubes 7 metres long. If the ratio be established between the volume of the liquid which passes up the pipe from bottom to top and the volume of steam which escapes from the top of the tube, it is found that this proportion is at

least as 1 to 1000. Globules are formed in the bottom of the tube, but when the volume and the speed of the steam are sufficient the liquid assumes a creeping motion, in the form of an extremely thin layer along the interior of the tube, whilst the steam circulates with a considerable speed of 25 metres per second in the axis of the tube (see Fig. 113). It will be realised that under these conditions evaporation is highly intensive and the liquids are evaporated under the best conditions which prevents them getting damaged. Practically in all cases where Kestner's evaporators have been applied superior products have been obtained, and the authors recommend this particularly interesting plant because by actual experience they have found such to be the case.

*Description.*—In a multiple effect evaporator on the Kestner principle, each effect consists of a calandria or steam jacket which contains a number of copper tubes. The tubes are usually expanded into the upper and lower tube plates. The lower box of the calandria is arranged so as to receive the incoming liquor and is designed so that it is possible to feed an equal quantity of liquor into each of the tubes. The evaporating tubes are from 5 to 7 metres long. The body or calandria "M" is constructed in the case of single effects in mild steel and in the case of multiple effects the first body is in mild steel, the others being in copper so that the whole of the liquor and vapours come in contact only with gun metal or copper.

At the top of the calandria is fitted a separator "S". This is arranged with a centrifugal baffle at the lower portion "D," so that the vapour and liquor on entering the separator are separated by means of this baffle: the vapour going upwards to the outlet "B" through the save-all "V" and the concentrated liquor leaving the separator at "L". This centrifugal baffle is so efficient that no entrainment of any kind takes place.

Fig. 113 shows a Kestner evaporator of this type working under atmospheric pressure. When working under vacuum the liquor flows out of the opening "L" and is carried down to the ground level by means of a pipe forming a barometric column, so that the concentrated liquor leaves without the aid of a pump. The vacuum is maintained in the separator "S" by means either of a wet air pump or by a barometric condenser, depending upon the conditions in the factory.

The heating steam enters through the opening "A" and the condensed steam leaves through the opening "E".

Independently of the above advantages Kestner's plant possesses moreover general simplicity in construction, few joints, consequently few leaks, a minimum of air leaks when working under vacuum, and great ease of regulation of the plant.



The inlet liquor to the opening "T" is controlled by means of a valve which regulates the density obtained in the last vessel. The floor space required is very small.

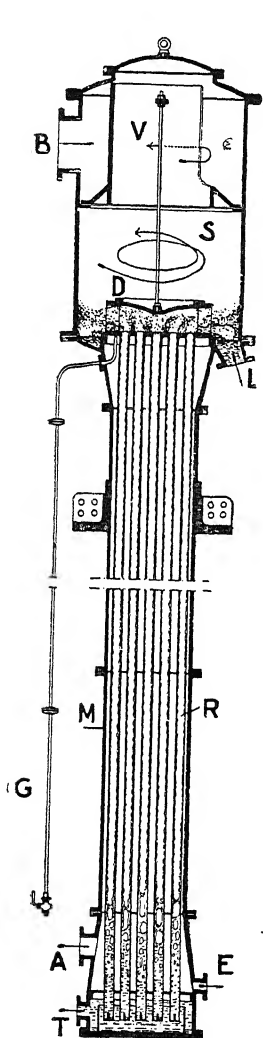


FIG. 113.—Section of a Kestner evaporator.

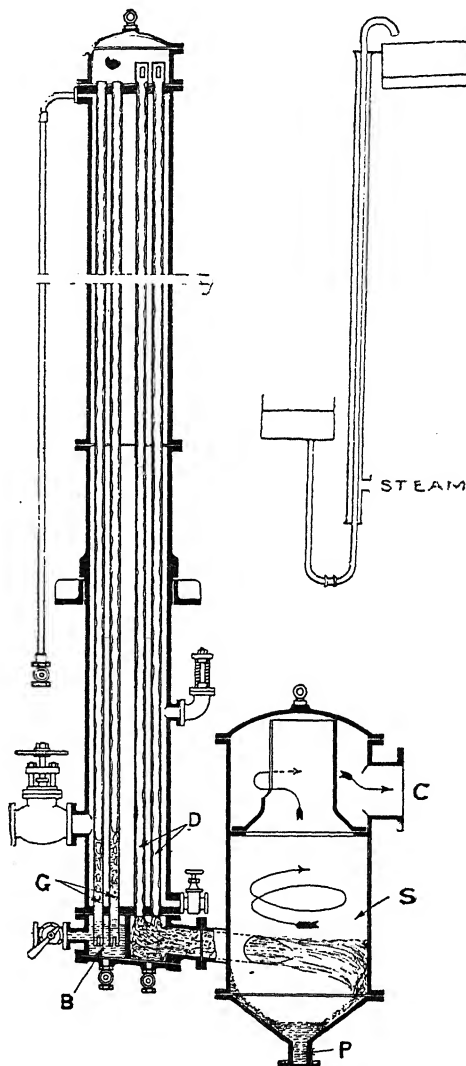


FIG. 114.—Kestner evaporator, simple effect.

*Washing.*—Ease of washing is a special feature of this plant, and enables it to maintain the maximum output. The section of a vessel (Fig. 113) shows that, as soon as the plant stops, the

liquid may be entirely evacuated. Each vessel may be washed very rapidly with the hot condensation water; such washing requiring about a quarter of an hour, and entailing no stoppage of the factory. The wash water circulates in the same direction as the concentration liquor; cleaning is, therefore, particularly efficacious, and the plant is very quickly in operation again, whilst, in all other evaporation systems, cleaning of the plant is a lengthy operation that cannot be done daily, which thus increases the difficulty. One or more Kestner vessels may be added to existing vessels. Their heating surface is thus increased and their output augmented, since to such evaporation plant there have been added one or several elements of much superior evaporative capacity. Even in heating by a steam coil, a Kestner evaporator, fed in the first instance by weak liquors, would supply steam to the coils to finish the concentration, and would thus realise very great economy of steam by establishing a group, working by double effect, the first element of which would be of great working capacity. Kestner's plant has numerous applications in different industries connected with concentration, and particularly is this the case with wood extracts, tanning extracts, logwood extracts, etc.

Fig. 114 shows a Kestner single effect evaporator that is used for producing solid extract. In installations where solid extract is required it is usual to first concentrate the liquor in a multiple effect under vacuum, and afterwards to finish in a vacuum pan which usually contains a stirrer. In the Kestner system, however, the time of contact is so short that it has been found possible to put in a single effect evaporator working non-vacuum, that is, exhausting to atmosphere, in which solid extract can be produced, and this type of evaporator is shown in Fig. 114. The principle on which it operates is as follows:—

The calandria is as described under Fig. 113, but the separator is arranged coupled to the lower box and is of the tangential type. The evaporator is built in accordance with the Kestner latest patents, the flow of liquor being as follows:—The liquor to be finally concentrated enters the box "B" through the inlet opening, it climbs up the climbing film tubes, descends through a set of falling film tubes, rises again in a further set of climbing film tubes and finally descends through the tubes "D" into the bottom box, whence it is discharged into a tangential separator. The arrangement of the tangential separator is such that complete separation of the liquor and vapour takes place, the liquor flowing out in a liquid condition. The moment this cools it is dry, containing only 10 to 15 per cent. moisture, the exact percentage depending on the class of extract and the conditions required.

The fact that experts have tested this product and found

that it contains no coloration due to its being concentrated in this way proves the enormous advantages of the Kestner system.

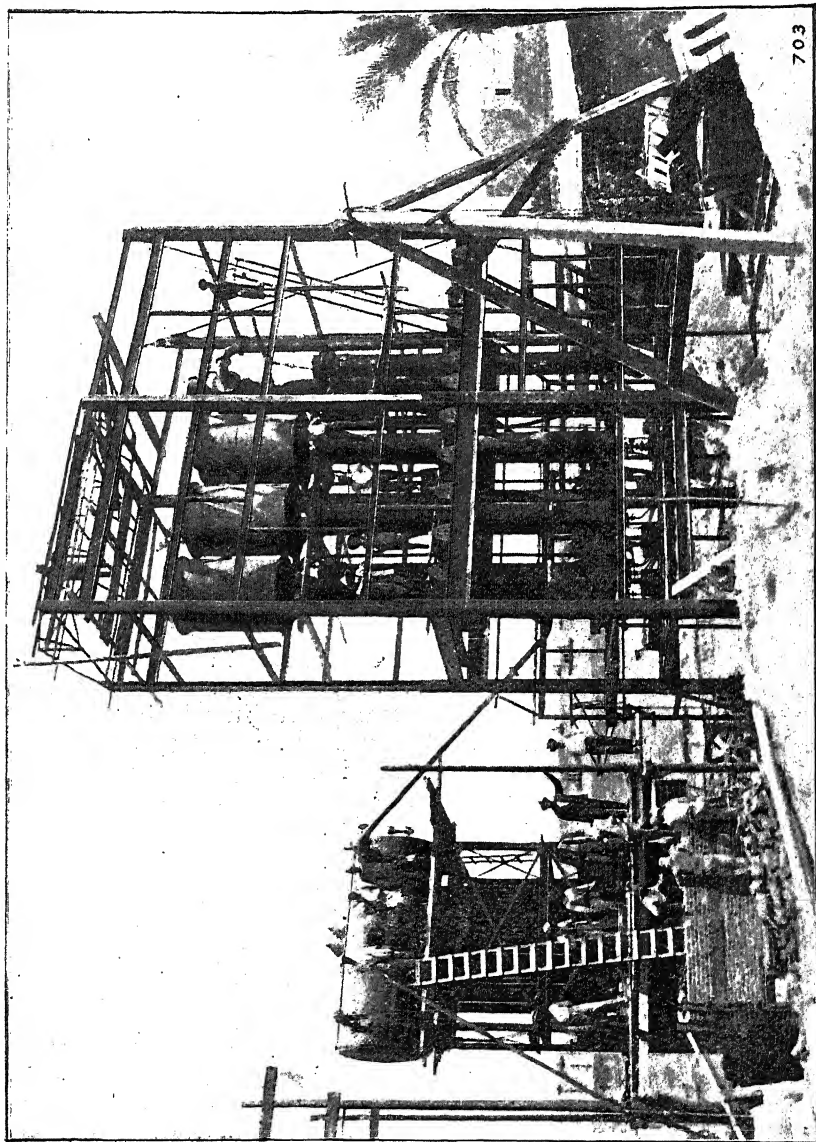


Fig. 115.—Kestner evaporator, quadruple effect,

Fig. 115 illustrates a Kestner quadruple effect evaporator working under vacuum.

Summing up, according to what has just been said, Kestner's evaporator is the apparatus best adapted, from every point of view, for the concentration of tannin and similar liquids, and the

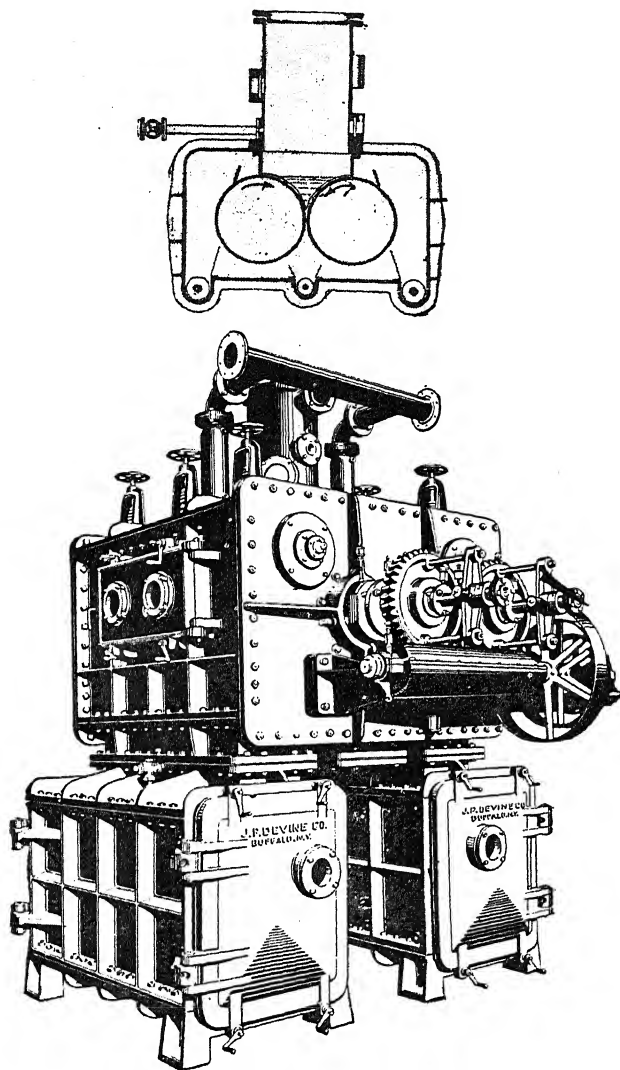


FIG. 116.—Devine Company's patent vacuum driers.

authors have described it at length with the object of drawing attention to its value in the manufactures with which we are dealing. Its efficiency has been abundantly proved.

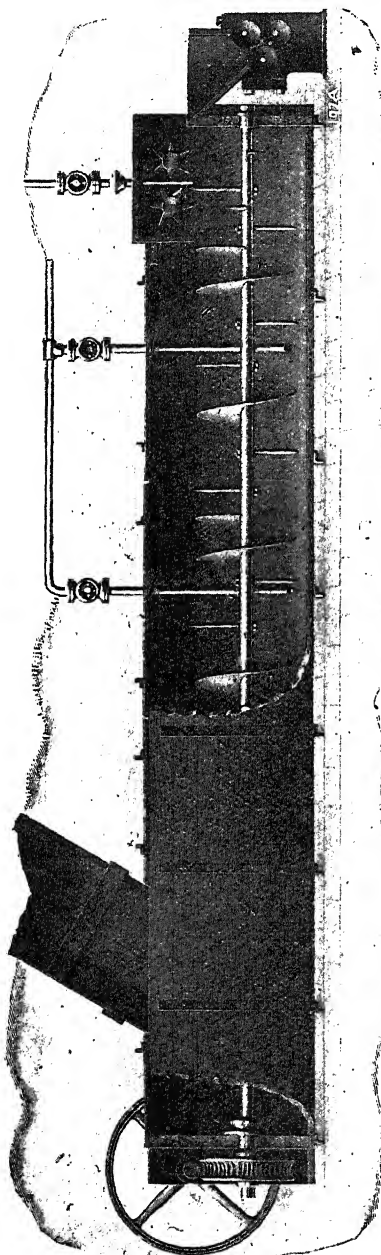
*J. P. Devine Company's Patent Vacuum Driers.*—The

FIG. 117.—Continuous "automat" extraction apparatus (Blair, Campbell &amp; McLean, Ltd.).

patented vacuum driers of the J. P. Devine Company, Buffalo (English agent, James Livingstone, Ltd., London), are used for evaporating tanning extracts and many other liquids. The single drum drier contains one hollow revolving drum or cylinder which is heated by steam or hot water. This drum revolves in the liquid to be dried and carries on its exposed surface a film not more than  $\frac{1}{125}$ th of an inch thick which is dried by one revolution and is removed by a scraper which is set so as to almost touch the drum, the films removed by it falling into receptacles placed below. The whole is encased in a special cast-iron cover which is made tight and in which a vacuum is kept up by means of a powerful vacuum pump.

The two drum drier (Fig. 116) has two drums working side by side, the liquid in this case being fed into a special patented form of hopper which delivers the liquid on to the surface of both drums. Wet materials containing as high as 88 per cent. of water are dried within 8 seconds without being overheated, the temperature of evaporation ranging from 96° to 117° F. according to the extent of the vacuum which may be equal to 28·3 to 26·8 inch.

In the thorough extraction of tanning materials with the minimum quantity of water, the countercurrent system presents considerable advantages, provided it can be worked satisfactorily with not too much handling of the material. This is carried out in a series of extraction vessels, the tanning material being conveyed in one direction by helical screws while the water passes in the opposite direction, becoming successively more concentrated as it passes from one extraction vessel to another, and meeting in its course less and less exhausted material until finally it acts upon unextracted material before passing out of the system. The patents of G. F. Bögel (Ger. Pat. 195,245, 1906) and W. Wiegand and R. Rieder (Fr. Pat. 386,820, 1908) are based on this system.

Fig. 117 shows a continuous "automat" extraction apparatus for extracting tanning materials, made by Messrs. Blair, Campbell & McLean, Ltd., of Glasgow.

## CHAPTER III

### METHOD OF USING CHESTNUT EXTRACTS IN TANNING.

THE tanner, unless he makes them himself, ought always to strive to secure the best quality of the chestnut extracts offered to him, which should always contain at 25° B. a minimum of 28 per cent. of tanning substances assimilable by the leather (analysed by the official method of the International Association of Leather Chemists), be soluble in water without more than  $\frac{1}{2}$  per cent. of insoluble and free from all trace of chemicals or other substances foreign to tannin. The purified brands, clarified and rendered soluble by absolutely mechanical processes, that is to say those in which all the insoluble extractive matter is eliminated (which, in ordinary extracts, is precipitated as soon as water is added and forms a mud suspended in the solution), should be preferred as giving the maximum yield of leather. This kind of extract, soluble in the cold state, is used for tanning heavy leather in the pit, namely, sole and belting leather; precise instructions will therefore be given as to its use in this special department of tanning later. The purified extracts, clarified by filtration of the liquor, according to the authors' instructions, and with addition of bisulphites, are especially adapted for semi-rapid or accelerated tanning and are even used for tanning calf, sheep and goat skins, into which they enter as adjuncts to, rather than as substitutes for, oak bark. The advantages of this method are esteemed for economical reasons in regard to cost of the tanning material, in the acceleration of the tanning, and in the yield of leather.

*Use of Extracts for Tanning in Pit.*—The better the quality of extract the better the result. However, generally speaking, their use begins with the moving of the hides from the suspenders. Some tanners taking their hides out of a liquor about 30° B., others up to 45° or 50° B. They then pass through several pits called layers in ranging degrees of strength. From these layers goods are dusted down with bark suitably ground, hides being placed grain to grain and dusted with the said bark between each and in liquor anything from 100° to 150° B.

*Method of Dusting.*—Cover very liberally with liquor consisting of a mixture of extract and liquor taken from the liquor

pits; bring this mixture to 100° B. first; dusting to 120° for the second, and 140° for the third, if three powders be given, as in the case of heavy leather or ox-hide for belting. Take care at the outset to fix a channel in the pit, by which the liquor can be drawn off when desired, either to replace it by other liquor or simply to displace it by pumping it up and redischarging into the same pit. After two, three, or four months (give the powders every month at the longest) the pit is turned or dry piled, then the liquor is withdrawn by the pump, or in any other way, in proportion as the hides are lifted and run to the liquor pits. The spent tan is also carried there. It will consequently be seen that in a very short time the liquor pits will become very rich. Instead of having in the front pits liquor weighing at the most 50° B., as it would be if bark were used alone, the liquor will very soon test 100° B. in the front pit, and in the tail pit, if the exhaustion has been done methodically, it will test 0 or very nearly so. What is to be done with this strong liquor? It can be used to form the bath in the handling which immediately precedes the laying in the pit. This bath is formed at 20° or 25°, according to the strength of the liquor. In the preceding rehandling, or in the vat, if only one handling be done, the bath is formed with liquor from the second liquor pit, the weakest liquors, when vatted, become stronger and stronger as the skins age in manufacture. By this method of working the pits an important economy in time may be realised, either because only two pits are given instead of three, or because the duration in each is abbreviated. By using 25° chestnut extract, simply clarified for tanning, ordinary coloured leather is obtained; by using clarified chestnut extract, rendered soluble, brighter coloured leathers are obtained.

*Tanning of Crust Leather.*—Extracts soluble in the cold are employed with barks titrating 10 tenths (1° B.) to nearly fill the pits, or for the initial bath (tanning by immersion), in order to increase the daily strength by 2° B., small additions of extract are made, so that in fifteen days a bath is obtained of 25° B., which gradually penetrates and passes through the leather, without either rendering it brittle or shrivelling it. The rapidity of tanning can evidently be accelerated by using a heating coil in the bath in which warm water of 30° to 35° C. circulates. This mild heat facilitates the assimilation of the tannin by the leather, swelling the skin, and producing crusts, soft and pliant to the touch. The addition of extract to the tanning baths or pits thus produces white crusts of high yield, provided, however, that they be dried in the dark as far as possible. The manipulation of the crusts during tanning can only be guided by practice and the routine of tanning adopted in each factory, the principles and the manner of working of which are different.



*Dissolving the Extracts.*—It is of the greatest importance that the extract to be used in tanning be uniformly distributed throughout the liquor to which it is added, because the extract, however pure and however soluble it may be in the cold, may remain imperfectly dissolved if the precautions incidental to its use be not taken. The tanner thus suffers a loss, and irregularity occurs in the results of his operations. The extract ought always to be added to the upper surface of the water or liquor of the vessel or pit, and not to the bottom, that is to say, the extract is to be run into the liquor slowly and not in a gush, taking care to stir constantly. The desired quantity of extract should never be discharged into the bottom of the reservoir or mixing vat, for water to be added subsequently on the top. It would be in vain to stir afterwards; complete solution would not be obtained. The best method of working is to heat in a vat to 30° to 35° C. (86° to 95° F.) a quantity of water at least equal to that of the extract to be used, condensed water is best for this purpose; then to pour the extract thereon, slowly stirring, as described above. This first solution, which works very well owing to the favourable temperature, ensures the perfect utilisation of the extract.

*History of Rapid Tanning.*—The idea of rapid tanning has had admirers in all ages, and has been the object of many researches; many tanners have dedicated thereto their knowledge, their time, and their money. Without reckoning the well-known names of Seguin, of Knoderer, of Worms and Balé, there is not a tanner, we believe, who has not made experiments with the object of reducing at any rate to some extent the time occupied in tanning which is certainly prolonged. Some Italian tanners in the time of the Italian wars tanned more or less rapidly, by using the "tumbler" even at that early date. It must be added, however, that the leathers so tanned were accepted as simply meeting the exigencies of the moment, and that slow tanning was returned to as soon as the urgent necessity had passed away. The system of Fratelli Durio (the famous tanners of Turin, who kindly allowed the authors to inspect their important and improved tannery during the Congress of Leather Chemists) is the outcome of a series of profound and rational researches on lines which had been already followed, a new milestone placed after other milestones on the road of progress of rapid tanning, but it may be also asserted that it is to the initiative of these tanners themselves that the true theory of rapid tanning and its definite adoption into actual practice are due. In 1881 they desired to buy the Italian rights of the Worms & Balé patent, based on the action of electricity, and before entering into further negotiations, they desired to make inquiries on the industrial value of the process, but after some

experiments, they concluded that the famous electric fluid exercised no influence on tanning. This patent did not, therefore, present any guarantee of success even as regards the very incomplete results yielded by the said process. Moreover, it is well known that all the tanneries which tested it at the time soon abandoned the process, and even the firm of Worms & Balé finally resorted to the system of Fratelli Durio, the principle of which was antecedent to their own, because in fact the so-called electric action on the leather turned out to be no other than the effect of the rotation or fall which took place in the fulling machines of the Turin tanners. It was, therefore, whilst pursuing experiments with extract in the tumbler that Messrs. Jacques and Segundo Durio, in 1882, almost on the point of being disheartened, finally solved the question of rapid tanning with high strength liquors; the old theory of time and strength of tan had to disappear from that day. Their idea was contested in the tanning world; but being forced to recognise its value, the critics tried to detract from it by attributing the invention to Knoderer (1850), asserting that if he had had extracts at his disposal, he would have tanned as well as Fratelli Durio. To make this assertion is not to know the tenor of Knoderer's patent, which states that this inventor used only non-concentrated, and therefore weak liquors, and that he, moreover, prescribed that the work should be done gradually, in order not to attack the skins too strongly at their exit from the river treatment. The system of Fratelli Durio is applicable to all kinds of skins and for all purposes: sole leather (smooth), upper leather, belts, saddlery. Any desired shade may be obtained at will. The different types of leathers produced by other tanners and enquired for by customers in different countries are very easily matched. The tanning is perfect and compact, the flower always soft and fine, finally the weight added owing to the tanning being more complete, is higher than in ordinary tanning. Like all patents, that of Fratelli Durio has had its improvers and its professors, who have hastily produced what they regarded as improved processes, by the addition of foreign matters to the extracts, or who have recommended the tanners to work *in vacuo* or under pressure. These have all met the fate which might be expected: they were still-born. The system of Fratelli Durio alone has continued to furnish to the whole world its indications of principle and simplicity, which have alone contributed to its success and which will impel its adoption by force of circumstance: other times, other manners. It is absolutely certain that if 20 per cent. of the tanners tanned with more rapid processes, a consumption of extract would result sufficient to render it necessary to double the output of the extract factories. That would be a real revolution in the tannery

and an evolution of the tannin industry, which, moreover, is capable of great development, provided that it is possible to find in India, in Australia, in Africa, in South America, and in the United States sufficient tanning materials capable of supplying it for an almost indefinite number of years. This appears quite possible when we reflect that the methodical exploitation of different woods may be renewed at intervals by careful cultivation, and the importation of part of the tannin material from foreign countries would counteract the deafforestation already spoken of in France and Corsica.

*Ultra-rapid Tanning.*—Into a rotary wooden “tumbler,” such as supplied by the tannery machine constructors, of 10,000 litres (2200 gallons) capacity, mounted on a hollow spindle with wooden blades in the interior, and driven by an alternate motion with a speed of ten turns a minute, the skins to be tanned are introduced through a bronze manhole. In the case of small skins, the tannin liquor contains 3 per cent. of tannin; it is generally made by dissolving mixed chestnut and quebracho or mimosa extract in water; for heavy leathers, the tannin liquor contains 5 to 8 per cent. To facilitate the penetration of the tannin into these heavy leathers they are first subjected to a radical treatment in river water, followed by a swelling bath, consisting of bark liquor, to which formic acid has been added in the proportion of 200 grammes per 100 kilogrammes of leather in bands. To neutralise the astringency of the chestnut tannin, it is well to use along with this extract some quebracho or mimosa, in proportions which vary with the origin and the nature of the skins to be tanned. In all cases the tanning of heavy leathers may be accomplished in forty-eight or sixty hours, that of small skins in eighteen or twenty-four hours. Each fulling tumbler may tan about 50 tons of leather for belts or soles yearly; 12 to 15 square metres of surface space suffice for its installation. It requires 2 h.p. This process, which does away with the pits, tan mills, sheds, and stitchers, with an expenditure of 1·8 to 2 kilogrammes of extract of 25° per kilogramme of finished leather, gives a 55 per cent. yield, and the cost of tanning a kilogramme of finished leather amounts only to 6 franc (5¼) per pound. In order that the skins may be regularly tanned the liquor must be maintained at a constant density for which purpose a communication is made between one of the hollow spindles of the tumbler and an elevated reservoir in which the extracts are mixed with water. After several successive operations the liquor from the tumbler should be evacuated and clarified before being used again with new liquors.

*Effect of Non-tannins on the Leather.*—Dr. J. Gordon Parker and J. R. Blockey<sup>1</sup> found in their experiments that non-

<sup>1</sup> *J.S.C.I.*, 1911, p. 1433.

tannins had a prejudicial effect in tanning, resulting in less tannin being absorbed and less weight of leather being obtained. They are also detrimental owing to their tendency to form acid products in the liquors. Gallic acid has a decided solvent action on the hide substance resulting also in loss of weight.

## CHAPTER IV

### MANUFACTURE AND USE OF OAK WOOD EXTRACT

*Oak Wood—Barks—Equipment and Plant of an Extract Factory—Method of Manufacture according to Albert Thompson and Emile Blin's Patent.*

*Oak Wood.*—The oak (*Quercus*), the bark of which is the tanning material *par excellence*, yields a wood containing 5 per cent. of tannin. Hartig found that the young wood, cut in the beginning of May, contains from 4 to 7 per cent. of tannin, whilst in winter the latter rises to 10 per cent. of the dry matter. The same author found, in the heart-wood of oak 160 years old, 12 to 14 per cent. of tannin. The percentage of tannin in the wood is maintained if, after felling, the wood is barked and sawn up; after several months the unbarked wood diminishes in strength, from the centre to the circumference. The alburnum contains little tannin; the lower parts of the tree contain the most. According to the experiments of Professor Henry of the French National School of Forestry, the following conclusions may be drawn: (1) The percentage of tannin progressively diminishes both in the bark and in the wood from the bottom to the top of the trunk, at least in the case of *Quercus robur*. (2) On a cross section it is always the alburnum which contains the least, generally from 1 to 3 per cent., then suddenly the tannin attains its maximum development in the peripheric layers of the duramen (6 to 10 per cent. in the oak, 13 to 15 per cent. in the chestnut), and continues to diminish, more or less regularly, to the centre. The large branches behave like the trunk. (3) Everything else being equal, the wood of an oak or a chestnut will be richer in tannin as its summit is more ample, more isolated, better illuminated, or in other words as its annual layers are wider. (4) A circular slice, exposed for a year to the weather, loses three-fourths of the tannin in its bark and alburnum, but half only of that in the wood. This difference is explained by the fact that in the bark and in the alburnum the tannin is dissolved in the sap of the cells, whilst in the duramen it impregnates the walls of all the tissues so intimately that a series of macerations on the water-bath, followed by several

pressings, is necessary to extract it. (5) It has been demonstrated that under the action of oxygen or of fungi such as the *polyporus sulphureus et igniarius*, which induce the first a red rot, the second a white rot in oak, the wood loses its tannin, whilst it preserves indefinitely a notable proportion of this principle, when these two causes of decay are eliminated. An enormous oak trunk of the quaternary epoch embedded in the soil of Nancy, for instance, still contained 2·36 per cent. of tannin.

*Varieties.*—The principal species yielding the different barks used in tanning or in the tannin industry are the common oak, *Quercus robur*, *Quercus pedunculata*, *Quercus ilex*, *Quercus rubra*. The evergreen oak (*Quercus ilex* L.), the bark of which is used for tanning light leathers. The white oak (*Quercus sessiliflor* Smith) and its tropical variety *Quercus pubescens*, the bark of which is specially used for tanning heavy sole leather. This bark gives a yield of 28 per cent. of 25° extract. It therefore requires 350 kilogrammes of this bark to produce 100 kilogrammes of 25° extract. The zeen oak (*Quercus mirbeckii* Duvieux). The kermes oak (*Quercus coccifera* L.), the roots of which yield *la garouille* which is used in tanning heavy leathers intended for belts. The cork oak (*Quercus suber* L.) (*Quercus occidentalis* Gay, in the Landes). The tannin from the bark is a catechol tannin sometimes known as quercin or quercitannic acid,  $C_{15}H_{12}O_9 \cdot 2H_2O$ , and differs from that contained in the wood.

*Percentage Strength of Tannin in some Varieties.*—White oak of La Drôme (Puygiron, near Monte Limar). These oaks of twenty to twenty-five years old, just beginning to form perfect wood or duramen, give the following percentages of tannin in different organs on analysis (see A in following table) B, Oak of d'Angers, C, Oak of de Mauleon.

TABLE XXIV.—DISTRIBUTION OF TANNIN IN DIFFERENT PARTS OF THE WOOD OF DIFFERENT VARIETIES OF THE OAK

	A.	B.	C.
Bark dried at 100° C. . . . .	10·8	8·53	7·74
Alburnum external . . . . .	2·2	1·95	1·98
„ internal . . . . .	1·7	3·18	1·74
Duramen external . . . . .	—	15·60	9·68
„ internal . . . . .	—	11·08	5·87

In 1894 Professor Trimble of Philadelphia examined the barks from a number of Indian oaks, and found that *Quercus incana* contained by far the largest amount of tannin, i.e. 23·36

per cent. The bark from *Quercus lamellosa* is used for tanning in Darjeeling (Sir George Watt, *The Commercial Products of India*).

The percentage of tannin in the bark, whether of white oak or of evergreen oak, always varies essentially with the source, but there is an especially propitious moment for collecting it, which affects this percentage, and as soon as it is packed in bags it must be protected from rain and intemperate weather which prevails during its collection. Tanners are especially interested in selecting this propitious moment for obtaining their annual stocks of different barks.

*Manufacture of Extract.*—Oak extract is manufactured in the same way as chestnut extract, except that the maceration of the chips in open vats is obligatory, and their clarification should be pushed to the extremity owing to the darker colour of the liquors. In France this manufacture is of little importance, looking to the small number of hectares at disposal for this exploitation, and especially to the poor yield of this wood, which does not exceed in a factory, working according to the latest improvements, 14 per cent. of extract. Certain factories use the top branches of oak which barely yield 7 per cent. of a 25° extract containing 22 to 25 per cent. of tannin. Other manufacturers use only for the manufacture of oak extract the blocks and the large branches of unbarked oak, of about 20 cm. in diameter, or the trunk split into logs of 50 to 60 kilogrammes (110 to 132 lb.). There is no profit in extracting the tannin from branches of 2 to 3 cm. in diameter, because, in the first place, they are too poor in this principle (2·2 to 2·5 per cent. of tannin), and in the second place, because they have an appreciable value as wood for charcoal. The twigs contain 4·7 to 6·6 per cent. of tannin. It would therefore be desirable for a wood distillery situated near cheap transport routes (canals) to add an extract factory, which would utilise, for its purposes, the oak brushwood, the value of which would enable the proprietors to realise a great economy on the purchase of their raw materials. Oak extract, employed in tanning as an adjunct, imparts to the leather a similar colour to that of bark-tanned leather; moreover, it may be used in larger proportion than chestnut extract, because it contains a number of products which have the most beneficial effect on the suppleness or pliancy of the leather (amylaceous, mucilaginous matter, etc.), and enable it to be used, not only in the tanning of sole leather (for which it is moreover employed) but also in the tanning of leather for uppers and other light leathers. The cost of oak extract, being about 20 francs per 100 kilogrammes (8s. per cwt.), it will be seen that its sale is, consequently, very limited. Thus the authors only know of two factories actually making pure oak

extract. The Hungarian and Russian extracts reach France at a more moderate price. As a brand of pure oak extract, the authors would quote that made by the oak extract company of Russia, whose works are situated at Kurenwka, near Kieff. This factory which dates from 1902, produces annually 6000 tons of liquid extract guaranteed to contain 27 per cent. of assimilable tannin. The average composition of these extracts is as follows:—

TABLE XXV.—SHOWING THE COMPOSITION OF A RUSSIAN BRAND OF PURE OAK EXTRACT

	Per cent.
Soluble tannin matter . . . . .	30.7
Non-tannins . . . . .	10.9
Water . . . . .	58
Insoluble . . . . .	0.4
	<hr/> 100.0 <hr/>

Degree Baumé at 18° C., 25.8. The authors may also quote as a genuine oak extract that manufactured by Miller's Standard Extract Co. at their Slavonia factory (exported through Fiume).

*Plant and Equipment of an Oak Extract Factory.*—The following is a specification for a factory of this nature, the basis of production being 4½ metric tons of 25° extract which works according to a patent described later. Two boilers with a heating surface of 140 square metres, gauged to six atmospheres; one Laboulais horizontal motor of 85 h.p., 90 revolutions; one horizontal motor of 10 h.p., 200 revolutions; one dynamo 110 volts, 30 ampères; switchboard for distributing to the electric light installation, comprising two arc lamps and thirty-eight lamps of 16 candle-power; belts; transmission shafting; pulleys; plumber blocks; gearing; lubricators; one cutter, 20 tons output; one cutter, 30 tons output; one cup elevator; eight vats for wood diffusion, each of 9000 litres (1980 gallons) capacity; nine vats for various manipulations of the liquor of 10,000, 4000, and 2000 litres (2200, 880, and 440 gallons) capacity; one filter press, Lump system; two filter presses with pumps and their respective motors, Johnson's system; two sets of copper concentration plant, Gouyer's system, with 70 square metres of heating surface; one copper vat of 1200 litres (264 gallons) capacity for the preparation of decolorisers; one wrought-iron hot water tank of 7300 litres (1606 gallons) capacity; one Lawrence copper refrigerating system; three wooden vats; one condensation pump, 25 cm. (25 tons capacity per hour); one elevation pump, 25 cm. capacity per hour; one feed pump, 3000 litres (660 gallons) capacity per hour; one centrifugal pump, 6000 litres capacity per hour; one air pump and condenser,



Worthington system; two sandstone grinding stones on cast-iron foundation for sharpening the cutters; one emery grinding stone on cast-iron foundation; iron, copper, and lead piping; copper taps and fittings; 300 metres of Décauville rails with six turn-tables, points; four tilting trucks with skips; three wood waggons; one wood barge of 15 tons; one Décauville crane on wooden staging for discharging vessels; one weighing machine of 10 metric tons load.

The following is given *in extenso* as a matter of curiosity: *Descriptive Memoir Lodged in Support of the Application for a Fifteen Years' Patent for Improvements in the Manufacture of Tannic Liquors by Albert Thompson and Emile Blin.*—The invention, which is the subject of the present application, relates to the manufacture of tanning liquors used in the tanning of skins for the preparation of leather.

The tanning liquors, generally obtained by diffusion in boiling water of certain woods rich in tannin, previously crushed to facilitate the extraction of the tannin principles which they contain, are commonly withdrawn from the diffusion vats when they reach 3° to 4° Baumé. These liquors are then clarified by means of substances amongst which acids (sulphuric acid, oxalic acid, etc.) intervene so as to precipitate or destroy the salts and coloured organic matter which they contain. This clarification effected, the liquors are then filtered to free them from the deposits induced by clarification, then they are finally concentrated in evaporation plant up to a density of 20°, 25°, 30° Baumé and more, according to the requirements of consumers. The tannin liquors, treated in this way by acids, always remain acid, and are impoverished in very appreciable proportion of their useful principles. Moreover, the oleaginous products employed in the majority of acid processes, to attenuate the destructive effect of these acids and to reimpart to the tannin liquors the velvety lustre which the latter remove, present many disadvantages, especially those which consist in forming spots, and in falsifying the density of the tannin liquor properly so called. Finally, the decolorisation of the tannin liquors, limited perforce by the loss of useful principles, due to the adoption of acid processes, has not as yet allowed tannin extracts of certain categories to be utilised, hence for the working of very light and very pale leathers there are not to be found at the present time tannin liquors sufficiently decolorised and of sufficient strength to be used for that kind of work. In our invention the tannin liquors, always obtained by diffusion, are clarified and decolorised without the use of acid or oleaginous product, and contain in proportion more utilisable principles than the tannin liquors treated by acid processes. They are neither acid, nor do they cause spots, and they contain no

substance capable of altering the natural density. Moreover, as great a decolorisation as consumers can desire is obtained by our process, and that without appreciably diminishing the percentage of useful principles. They possess indisputable qualities from the point of view of tanning leather. All these results being obtained without destroying the natural velvety lustre of the tannin liquors and without resource to the use of acids. Our invention rests on the following researches : mineral acids, sulphuric acid, for example, precipitate lime salts, and destroy certain organic principles present in the tannin liquors, and thus decolorise them. But these acids have a destructive effect on the tannin, and cause its energetic oxidation, especially when warm, an appreciable quantity of tannic acid being transformed during concentration into gallic acid. Now it must not be forgotten that the products of oxidation of physiological tannin neither precipitate gelatine nor albumen. They are therefore useless. On the other hand, they give black colorations with salts of copper and salts of iron, and are therefore injurious. A series of methodical researches has caused us to resort to the use of vegetable alkaloids, preferably the vegetable bases naturally contained in quinquinas, quinine, quinidine, cinchonine, cinchonidine, and their isomers or derivatives. We use either one of the alkaloids separately, or a mixture of two or more bases as need be. (1) These bases, in the free state, or in the condition of salts, are precipitated by pure physiological tannin, and the precipitate of tannate is soluble in an excess of tannin or organic acid. (2) In tannin liquors the precipitates formed by these bases, or their salts, do not redissolve in an excess of liquor. It was, therefore, to be foreseen that decolorisation, produced by this method, would precipitate but very little pure tannin. Experience fully confirmed the fact, and our liquors are much richer in tannin material than those clarified by other processes. Besides they are in no way damaged by decolorisation, and retain their natural velvety lustre, so much sought after by tanners. Finally, the greater part of the vegetable alkaloids being found in the deposit from the clarification, we recover them by one of the processes used in the extraction of quinquina. We applied the following process: The drained precipitate is treated warm by water acidulated to the extent of 5 parts in 1000 with hydrochloric acid. The liquor is filtered and treated with milk of lime, gauged in the proportion of 10 grammes of quicklime per litre of hydrochloric acid liquor. The alkaloids are precipitated by the excess of lime. The precipitate is collected, washed with cold water, then treated with a slight excess of water acidulated by sulphuric acid. The acid liquor containing the alkaloids is filtered, decolorised warm by animal black, again filtered and neutralised

with quinine or one of the other alkaloids precipitated by carbonate of soda in a portion of the liquor. It only remains to titrate the solution obtained. It is to be understood that we reserve the right of applying such process of extraction as we may desire, having only pointed out the above process to show the economy of our invention from a commercial point of view.

*Method of Working.*—The tannin liquor as it comes from the diffusion vat has a density varying commercially from 3° to 4° Baumé. (The strength is obtained naturally as desired.) It is allowed to cool to the surrounding temperature; when cool an aqueous solution of the alkaloidal salts of quinquina or of these pure alkaloids, as occasion may require, is run into the tannin liquor, stirring energetically for a few minutes (five minutes suffice). The salts of the alkaloids enter into this operation in the proportion of 1, 2, or 3 kilogrammes per metric ton of extract brought to 20° Baumé, according to the decolorisation which it is desired to obtain. It is evident that less or greater quantities than those indicated may be used according to the result which it is desired to obtain. Under the action of these alkaloids the coloured or extraneous matters in the tannin, as well as a certain quantity of the latter, are precipitated along with the alkaloids, etc., leaving the liquor with its glossy appearance, so much sought after by consumers. We ought to say that the same results are obtained, whatever the temperature. But as warm working operates much more slowly, this method appears to us economically less practical, and that is why we have preferably indicated cold treatment in the first place, which is more rapid the lower the temperature. We may recall that in our process no dangerous caustic or poisonous substance is used, and that we cause the greater part of the alkaloids used to re-enter into the manufacture.

*Résumé.*—Summing up, we claim as our invention and our exclusive property: (1) The process which consists in using quinine alkaloids, either mixed or separately, for the clarification and decolorisation of tannin liquors obtained by diffusion. The said alkaloids pure or in the state of saline combination used in proportion varying with the decolorisation which it is desired to obtain, but in sufficient quantity, according to us, in a maximum proportion of 4 kilogrammes per metric ton of liquor brought to 20° Baumé. This proportion enabling almost white tannic extracts to be obtained and used indifferently, hot or cold, without distinction of degree of temperature, the said process having for its object the precipitation without the aid of an acid of the coloured or foreign substances which may exist in tannin liquors, whilst at the same time preserving to these latter, without the aid of any oleaginous or other greasy body, the glossy appearance which it ought to have for con-

sumption and which it naturally possesses. (2) As a new commercial product the tannic liquor presenting the following characteristics: free from acid exempt from any oleaginous or greasy body, preserving naturally its velvety and glossy appearance, possessing, notwithstanding its decolorisation having been pushed to an extreme point, a percentage of tannin higher than that obtained with acid processes, the said product enabling the tanning of skins to be effected under better conditions and extending its use to certain classes of leather up to now deprived of this style of tanning. Moreover, this tannin liquor possesses as an essential quality the characteristic that it is less sensitive to the oxidising influences of the air than that obtained by acid processes, which always contain gallic acid destitute of tanning power, neither precipitating gelatin nor albumen, and injurious because they give dark colorations with metallic salts.

*For* THOMPSON and BLIN,  
(Signed) ARMENGAUD aîné.

Seen to be annexed to the patent of fifteen years taken 28 July, 1899, by Thompson and Blin. Paris, 13 November, 1899.

## CHAPTER V

### MANUFACTURE AND USE OF QUEBRACHO EXTRACT

*Quebracho Wood. Generalities.*—Quebracho colorada (*Quebrachia lorentzii*) is a tree of the family of Anacardiaceæ, or sumach family, growing in the Argentine Republic, Bolivia, Uruguay, Brazil, Guiana, but it is especially in Paraguay where its exploitation is at present carried on (several factories have been installed there since 1902), as well as in the Argentine Republic to the north of Santa Fé, on the Rio Parana, and at Véra, which is 250 kilometres from Santa Fé, where there are important exploitations of quebracho colorado for the manufacture of dry extracts on the spot. Its importation into France dates from 1873. It is a very durable, hard, red wood of average elasticity, even slightly brittle. Its density is 1.27 to 1.38 and weighs 78 lb. per cubic foot.

The name quebracho is applied, not only to true quebracho (*Quebrachia lorentzii*) but also to several other trees among which may be mentioned the "white" quebracho (*Aspidospermum quebracho-blanco*) and red quebracho (*A. quebracho-colorada*) which belong to a different family of plants (Apocynaceæ). The true quebracho is found growing over a very large area in South America, not in large numbers in any particular place, but as isolated trees in the open forest regions, there being usually not more than four or five trees to the acre. The total possible yield of wood is estimated at 168,000,000 tons, while the annual consumption does not amount to more than 1,000,000 tons. The heartwood of the tree contains 20 to 24 per cent. of tannin, the sapwood 3 to 4 per cent., and the bark 6 to 8 per cent., only the heartwood being used as a rule. Santiago del Estero and Santa Fé, Argentina, are the districts where the tree attains its maximum size and the wood is richest in tannin.<sup>1</sup> On analysis it yields:—

TABLE XXVI.—SHOWING THE PROXIMATE COMPOSITION OF QUEBRACHO WOOD

	Per cent.
Water . . . . .	14
Tannin calculated as dry matter . . . . .	20
Extractive matter . . . . .	10
Woody fibre . . . . .	55

<sup>1</sup> C. D. Mell and W. D. Bush, U.S. Dept. Agric. Forest Service. Circular 202.

Quebracho contains, beside extractive matters, colouring principles difficult to eliminate, and which have greatly hindered its use, because they impart to the leather an unpleasant red colour, but which at the present day are removed by chemical treatment which clarifies and decolorises them. The bark of the wood does not tan leather; it contains only 1.55 to 2.25 per cent. of tannin (Villon). This bark has often been confused with that from the curupay (*Acacia curupy*). Other woods resemble quebracho in hardness and in appearance, but do not contain tannin. The tan wood called tanho (*Aspidospermum churneum*) contains 7 per cent. of tannin; the peroba (*A. peroba*) 5 per cent., peyma amarella (*A. sessiflora*) 10 per cent., the fever bark 4 per cent.

The tannin in quebracho (quebrachitanic acid) is somewhat exceptional, being only sparingly soluble in water and depositing from hot solutions on cooling. According to Arata it has the formula  $C_{24}H_{24}O_{10}$ , and Perkin and Everest (*The Natural Organic Colouring Matters*) state that it contains catechol and phloroglucinol nuclei.

*Manufacture.*—Quebracho extract is made in the same way as chestnut or oak extracts. The wood is cut into chips, then macerated in wooden vats in the open air or in autoclaves. The quebracho liquors so obtained are clarified and concentrated by triple effect to 25° or 30° B. or evaporated to dryness. In normal manufacture, and according to the kind of quebracho wood treated, the yield in 25° extract is from 38 to 45 per cent. of the wood treated. The disadvantage under which the French manufacturers of this extract are now working at the present time as compared with the tropical countries will be understood, especially since the South American factories work normally, if we bear in mind that the average price per ton of quebracho wood at Havre fluctuated between 115 and 117 francs (£4 12s. to £4 13s. 7d.) delivered, in 1908, but which is constantly rising. If there be added to the cost of the raw materials (*i.e.* 250 kilogrammes of wood) to manufacture 100 kilogrammes of extract at 25° a minimum of 5 francs for working expenses, special allowance being made for the difficulty of cutting and handling the wood, it will be seen that there is no advantage in manufacturing quebracho extract in France, and that tanners would do better to purchase for their use dry Argentine extract or some other brand, and to prepare for themselves a liquid 25° extract with a net profit of 4 francs per 100 kilogrammes. The cost price of French manufacturers cannot be materially lowered, whilst that of the tropical extractors will undoubtedly fall through over-production. Besides, the purity and the percentage of tannin in these South American extracts are now well known. It will suffice to give here the composition of known brands.

TABLE XXVII.—SHOWING THE PERCENTAGE COMPOSITION OF QUEBRACHO WOOD EXTRACT

	A.	B.	C.	D.	E.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Tannin matter . . .	64.9	69.60	64.8	45.65	31.4
Non-tannins . . .	4.9	9.60	16.4	5.05	9.4
Water . . .	13.5	13.12	17.7	46.70	56.0
Insoluble . . .	16.7	7.68	1.1	2.60	3.2
Total . . .	100.0	100.00	100.0	100.00	100.0

A, Harteneck Hermanos of Buenos Ayres; B, Casada; C, G. B. M. decolorised; D, Pasty extract decolorised; E, Average composition of liquid 25° extract of French manufacture.

The authors have made numerous tests with 25° quebracho extract, using dry extracts of South American origin, using the same amount of alkaline sulphites as that indicated by the composition of a 25° French extract, and have practically demonstrated that 100 kilogrammes of dry extract yield a minimum of 225 kilogrammes of 25° extract, completely soluble in the cold and quite assimilable by the leather, whilst yielding quite as good a tint as any decolorised.

*Results of the Authors' Sulphitation Experiments.*—The following are the results obtained by simply varying the proportion of alkaline sulphites used per 100 kilogrammes of 25° extract :—

TABLE XXVIII.—SHOWING RESULTS OF EXPERIMENTS ON SULPHITATION QUEBRACHO EXTRACT

Sulphite per cent.	11.	13.	15.	18.	20 to 25.
Tannin matter . . . . .	38.2	37.8	36.6	34.8	32.0
Non-tannins . . . . .	6.2	6.4	7.8	8.2	10.6
Water . . . . .	55.6	55.8	57.0	57.0	57.4
Insoluble . . . . .	0.0	0.0	0.0	0.0	0.0
Total . . . . .	100.0	100.0	100.0	100.0	100.0
Total soluble per cent. . . . .	44.4	44.2	44.4	43.0	42.6
Yield per cent. in 25° extract . . . .	180.0	150.0	200.0	204.0	210.0

It will be seen that the percentage of "soluble" does not vary more than 2 per cent. from one experiment to another, and that in spite of the increase in the addition of sulphite, the percentage of tannin decreases. The tanner, therefore, has no

interest in an extract sulphited in the ratio of 20 to 25 per cent., but rather in an extract sulphited to a minimum extent, *i.e.* containing a maximum of soluble tannin. Now, as that sulphited to the extent of 11 per cent. contains no insoluble, its value is easily demonstrated in good tanning, which should exclude a large quantity of sulphites, as being liable to injure the quality of the leather, owing to the difficulty in eliminating it. Moreover, 25° quebracho extract, sulphited only to the extent of 5 per cent., produces leathers with a higher yield than those tanned with extracts sulphited to a greater extent, whilst still retaining much more suppleness. This class of extract is made directly in a single vessel (Fig. 96), by running in the dry extract<sup>1</sup> all at once, and the right amount of water; the mass is then heated for some hours, after which the corresponding amount of 25° extract, perfectly soluble in the cold, is run off.

As a matter of interest, there is given below a copy of a patent for a "Process of converting dyewood and tanning extracts into new products of greater industrial value by the action of the bisulphites, sulphites, and hydrosulphites of soda, potash," etc. Application made by La Société Lepetit, Dollfus et Gansser, No. 255,698 of April 20, 1896. (See also Eng. Pat. 8582, 1896.)

*Descriptive Memorandum.*—Of late years the action of alkaline sulphites on bodies of the aromatic series has been repeatedly investigated. We quote as examples the German patents 56,058 and 76,458 of Fischesser (Wagner's *Jahresb. der Chemischen Industrie*, 1895, p. 602), the German patents 86,097 of February 18, 1895; an application for patent of the Farbwerke Hoechst, 1895, according to which a reaction, previously investigated by Piria, is applied (Liebig's *Annalen*, v., 78, p. 31), *viz.* the action of sulphites on nitro-naphthalene. We have investigated the action of sulphites and bisulphites on dyewood extracts, *e.g.* yellow wood, fustic, quercitron extracts and on tannin extracts, *e.g.* sumac, quebracho, chestnut, gambier, etc., and we have found that under certain conditions new products are formed, which differ essentially from those employed as raw material and are of great commercial value. These new products and their manufacture are the object of the present application for patent, and we explain our process by the following examples:—

*Example I. Preparation of a New Colouring Substance by the Action of Bisulphite of Soda on Yellow Wood Extract.*—We heat in an autoclave, at a temperature of 110° to 115° C., for eight hours, 300 kilogrammes of 28° yellow wood extract and

<sup>1</sup>There are now on the market brands of soluble quebracho containing only about 5 per cent. of sulphite and sufficiently decolorised to be used directly in the tannery.



100 kilogrammes of sodium bisulphite solution of 35° B.; the yellow extract is then converted into a pale yellow, very dense mass, which has the appearance of pure *morin*; it consists of microscopic needles, difficultly soluble even in hot water and representing an addition product similar to the addition compounds which aldehydes give with bisulphites. Acids easily liberate sulphurous acid from it, but do not, however, regenerate yellow extract with all its properties. The product so obtained, used such as it is, or neutralised by carbonate of soda, or well purified by washing with cold water, dyes cotton and wool on mordants, imparting thereto much brighter, deeper, and purer tints than Cuba extracts; it gives pure yellow tones on alumina in calico printing.

*Example II. Preparation of a New Colouring Substance by the Action of Bisulphite of Soda on Fustic Extract.*—We heat in an autoclave, at a temperature of 145° to 150° C., for eight hours, 300 kilogrammes of 28° B. fustic extract and 100 kilogrammes of bisulphite of soda solution of 35° B. The fustic extract is converted into a dense mass of a very pale, greyish, yellow colour, almost white when dry, very slightly soluble in hot water, soluble to a fine bright yellow in alkalis. The product differs from the fustic extract used, in the same way as the derivative of the yellow wood extract differs from the extract itself, *i.e.* it yields on wool and cotton fixed on mordants much purer and much brighter tints.

*Example III. Conversion of Quercitron Extract into an Easily Soluble Dye of Greater Intensity.*—We heat in an autoclave, to a temperature of about 150° C., from six to eight hours, 300 kilogrammes of 25° B. quercitron extract and 100 kilogrammes of bisulphite of soda solution of 35° B. The product obtained differs from the pure quercitron used, in so far that it dissolves with the greatest facility in cold water, a very desirable property in calico printing, and by the fact that it possesses a much more intensive colouring power. The action of the bisulphite, in this example, has a certain analogy with the action of dilute acids on quercitron extract, so as to decompose it into sugar and colouring principles, but the decomposition of glucoside by boiling dilute acids being accompanied by the formation of secondary bodies, the product so obtained has not the purity of tone which can be obtained by means of bisulphite.

*Example IV. Conversion of Quebracho Extracts, generally Imperfectly Soluble in Water into a Tannin Extract Completely Soluble in Cold Water.*—(a) We heat in an autoclave, for six hours, at 140° to 150° C., 300 kilogrammes of quebracho extract of 25° B., and 80 kilogrammes of bisulphite of soda solution of 35° B.

(b) We heat in a jacketed pan, fitted with an agitator and

heated by steam of one and a half to three atmospheres, for eight to ten hours, with constant agitation, 300 kilogrammes of quebracho extract and 100 kilogrammes of bisulphite of soda, or of neutral sulphite of soda solution of 30° B., or 130 kilogrammes of hydrosulphite of soda of 20° B.

(c) Instead of converting quebracho extract into a soluble product, the latter may be obtained directly by extracting quebracho wood, with or without pressure, adding for every 100 kilogrammes of wood 12 to 15 kilogrammes of bisulphite or sulphite of soda to the water used to extract the wood. The extract obtained according to (a), (b), (c) presents the same properties: it is more fluid than the present commercial quebracho extracts, dissolves easily in cold water without producing any insoluble deposit, it tans skin rapidly and imparts to it slightly rose tints, recalling those produced by mimosa bark, so highly prized by connoisseurs; moreover, the leather has a remarkable suppleness which is not obtained with ordinary quebracho. Naturally the time, the temperature, and the proportions given in the present application for patent vary within rather wide limits. Instead of bisulphite of soda those of ammonia and potash may be used. The application to Persian berries, wood, hemlock, catechu, *pigou*, etc., is the same as that described in the examples quoted. Summing up, we claim as our exclusive property: (1) The process consisting in heating dyewood extracts or extracts for tanneries, such as yellow wood, fustic, quercitron, quebracho, hemlock, chestnut, etc., extracts, with sulphurous acid, alkaline bisulphites, sulphites, and hydrosulphites, in an autoclave to temperatures higher than 100° C. or in the open air. (2) The products obtained by this process. (3) The application of these products to dyeing and calico printing and tanning or to the preparation of new dyes.

*Copy of the Certificate of Addition to the Patent, No. 255,698 April 20, 1896, for "A process of converting dyewood and tannin extracts into new products of greater commercial value, by the action of the bisulphites, sulphites, or hydrosulphites of soda, potash," etc. Application made by La Société Lepetit, Dollfus et Gansser.*

*Descriptive Memorandum.*—In our chief patent, No. 255,698, of April 20, 1896, we described the preparation of new tinctorial products, bisulphite compounds of the colouring principles of yellow wood and fustic, and also the conversion of ordinary quebracho, hemlock, and pine extracts, soluble with difficulty in the cold, into easily soluble extracts, and we mentioned the altogether special importance of this slightly soluble extract for the different purposes of rapid tanning. In continuing our experiments on the preparation of these extracts, we have found that they are rendered soluble on heating quebracho and hem-

lock extracts with bisulphites and sulphites for a somewhat long time, a portion of the sulphurous acid being expelled, neutral sulphites with an alkaline reaction are formed, which facilitate the solution of the resinous principles of the extracts. The excess of sulphurous acid in contact with the extract during the period of treatment prevents any oxidation, and induces at the same time a certain decolorisation of the extract, owing to its reducing action. We have found that soluble extracts are also obtained when alkaline bisulphites, sulphites, or hydrosulphites are wholly or partially replaced by some alkaline salts of sodium, potassium or ammonium, such as borates, carbonates, bicarbonates, phosphates, lactates, or sulphides, or hydroxides of sodium, potassium or ammonium. It is always necessary to render the extracts soluble by working in the hot condition. But the operation is a very short one (instead of lasting seven to eight hours in the conditions described in our chief patent), and requires a smaller quantity of added products for the conversion into soluble extracts. It is always advisable to add to the products, which render the extracts soluble, a certain quantity of reducing substances, such as sulphites, bisulphites, hydrosulphites or sulphides, so to prevent any oxidation; but such procedure is not absolutely necessary.

*Example.*—(a) 1000 kilogrammes of 26° B. quebracho extract are heated in a steam-jacketed pan fitted with an agitator up to 90° or 100° C., and ammonia, about 76 kilogrammes, diluted with its own weight of water, added gradually, with or without sulphide of soda; the stirring is continued until a sample of the mass dissolves in much cold water to yield an almost limpid solution, *i.e.* only depositing after some time a slight flocculent precipitate, because it is found preferable not to push the conversion too far.

(b) 1000 kilogrammes of 26° B. quebracho extract are similarly treated with 75 kilogrammes of caustic soda of 10° B. and 20 kilogrammes of sulphate of soda of 30° B.

(c) 1000 kilogrammes of quebracho extract are heated in a rather large pan to 95° to 100° C., and 80 kilogrammes of soda crystals dissolved in 100 litres of hot water, added gradually with agitation, or an equivalent quantity of potash or bicarbonate of soda, or potash or ammonia, regulating the temperature and the addition of the alkaline solution, so that the mass does not prime; heating is continued until a sample exhibits the solubility described in (a).

Summing up, we purpose to annex to our chief patent, and claim as our absolute and exclusive property:—

I. (a) The conversion of tannin extracts soluble with difficulty in cold water, such as quebracho, hemlock, and pine extracts, into products more easily soluble, by means of appro-

priate hot treatment, by the hydroxides, sulphides or salts with an alkaline reaction of sodium, potassium or ammonium, in the presence or absence of bisulphites, sulphites or hydrosulphites.

(b) The preparation of soluble extracts, consisting in extracting quebracho wood or hemlock or European pine bark with water containing the products enumerated in (a).

(c) The processes described in (a) and (b) applied to mixtures containing other tannin matters, beyond those enumerated in (a) and (b).

II. The application of easily soluble extracts in tanning, alone or in admixture.

III. The products obtained according to I. (a), (b), (c).

In 1917 a combine of the quebracho extract manufacturers in Argentina and Paraguay was formed with the object of regulating production and thus stabilising prices which had fluctuated considerably in previous years. Six companies in Argentina and four companies in Paraguay joined this combine, their total output being 165,000 metric tons of extract. The capital invested in the quebracho industry in Argentina alone is estimated at 10,000,000 pesos currency. The exports of quebracho extract increased from 80,153 metric tons in 1914 to 100,213 metric tons in 1915 (*Board of Trade Journal*, Feb. 15, 1917).

A solid extract containing 64 per cent. of tannin, estimated by the shake method, is now manufactured in the Argentine by The Forestal Land, Timber, and Railways Co. Ltd., London and Buenos Aires.

*Method of Application in Tanneries.*—The solution of quebracho extract (only those soluble in the cold are meant) ought always to be carried out, as already described, in regard to chestnut extract, *i.e.* run the extract into the water, preferably at 35° to 40° C., or into the bark liquor intended for tanning.

*Tanning of Sheep Skins.*—It requires about 4 kilogrammes of quebracho tannin to tan twelve finished sheep skins of 8 kilogrammes. This quantity of skins is laid in a vat containing 50 to 60 litres (11 to 13·2 gallons) of weak bark liquor, to which there are added:—

TABLE XXIX.—SHOWING THE PROGRESSIVE DAILY STRENGTHENING OF WEAK BARK LIQUOR IN THE TANNING OF SHEEP SKINS BY QUEBRACHO EXTRACT

First day, morning, first addition . . . . .	800	grammes of tannin
" " two hours after, second addition . . . . .	800	" "
Second day, morning, first addition . . . . .	800	" "
" " two hours after, second addition . . . . .	800	" "
Third day, one addition . . . . .	800	" "
	4000	" "

The skins ought to remain in contact with the bath liquor three or four days, they are then withdrawn, drained on the

horse, washed in clean water, again drained, and finally laid out to dry screened from light. During the first three days of tanning the skins are agitated with a paddle mill; the last three days it suffices to stir the skins about three times throughout the day.

*Tanning of Calf Leather.*—To tan a calf skin of about 3 kilogrammes, it requires about 3 kilogrammes of quebracho dissolved in 25 litres of weak bark liquor. The skins are agitated in vats from five to six days, during which additions of extract are made, in the morning and afternoon, at the rate of 250 to 500 grammes, up to the completion of 3 kilogrammes. According to the nature of the skins and their thickness, the duration of the tanning may be prolonged a few days; the tanner himself is the best judge in such a case. In any case, when the skins are tanned, they are drained on a "horse," washed in clean water, then drained and finally laid out to dry slowly.

*Tanning of Heavy Leather.*—Quebracho extract may also be used for tanning heavy leather, provided that it is employed only in the rehandlings, and in gradually increasing proportion, which may rise rather high.

*Remarks.*—In commencing tanning operations, it is indispensable to use weak and already used bark liquors. The baths, from which the tanned leather has been withdrawn, may serve as an initial bath for new leather before it is put into a new bath; this is a method of utilising the tannin contained therein. It is evident that it is necessary to agitate the skins after each addition of extract, which ought to be previously diluted with bark liquor; the success of the tanning process depends on this work being done gradually and judiciously.

With regard to the influence of bisulphites in sulphited extracts on the tanning of leather, Parker and Gansser,<sup>1</sup> and also R. Lepetit and C. C. Satta,<sup>2</sup> have shown by numerous experiments that no injurious effect on the leather is produced. The sulphites being largely converted into sulphates by oxidation, but the proportion of free sulphuric acid was very slight.

<sup>1</sup> *Jour. Soc. Chem. Indt.*, 1901, p. 1085.

<sup>2</sup> *Collegium*, 1904, pp. 311, 317.

## CHAPTER VI

### MANUFACTURE AND USE OF SUMAC EXTRACT

(Obtained from various species of the Genus *Rhus* (order Terebinthacea))

*Leaf Sumac*.—The following varieties are found in commerce: *Sicilian sumac* (*Rhus Coriaria*), which contains from 16 to 24 per cent. of tannin, is the most esteemed, and ought to be specified for the manufacture of extracts (*sommaco masculino* or male sumac up to 27 per cent., *summaco femminello* not so rich); *Italian sumac*, which contains from 13 to 18 per cent.; *Spanish sumac* (collected in the provinces of Malaga or the districts of Priego, of Malino, of Valladolid) is a somewhat esteemed variety, which contains 12 to 15 per cent. of tannin; *Tyrol sumac*, very odoriferous; *Venetian or Turkish sumac* from *Rhus cotinus* contains 16 to 17 per cent. of tannin; French or Donazère sumac, containing 13 to 14 per cent. of tannin, is prepared in the valley of the Rhone, in the form of a dark green powder, the smell of which recalls that of the leather; *Redon sumac*, which grows throughout the whole of the South of France; its tannin content equals that of the preceding; *American sumac*, much used in admixture with Sicilian sumac by Morocco manufacturers and for the tanning of buff leather; it averages 16 to 20 per cent. of tannin; *Virginian sumac*, the tannin content of which is variable. Each of these varieties contain a different tannic acid, but according to Stenhouse, the tannic acid of Sicilian sumac is identical with gallo-tannic acid. In damaged sumacs or those which have been warehoused too long in badly ventilated stores, the greater part of the tannic acid is transformed into gallic acid and glucose, with a consequent deepening of the colour of the solutions.

Other tanning materials known as sumach are *French sumac*, the leaves of *Coriaria myrtifolia* which contain, according to Procter, 15.6 per cent. of tannin. *Russian sumac*, the leaves of *Arctostaphylos uva ursi* (Bearberry) containing about 14 per cent. of a gallotannin (Perkin) and *Cape sumac* from *Colpoon compressum* (Berg), a small bushy plant, the

leaves of which, according to Procter, contain 23 per cent. of tannin.<sup>1</sup>

In the United States a number of species of sumach plants are found, the leaves being used in large quantities for tanning purposes, the following have been identified: *Rhus typhina* or Virginian sumac with 10 to 18 per cent. of tannin; *R. cotonoides*, 21 per cent.; *R. semialata*, 5 per cent.; *R. aromatica*, 13 per cent. (Procter); *R. metopium*, 8.2 per cent. (Perkin); *R. Copallina*, *R. pumilia*, 16.99 per cent.; *R. toxicodendron*, and *R. glabra*, 23.56 per cent.<sup>1</sup>

The following analyses by F. Austyn Blockey are of interest, the samples having been collected personally by the late Professor Trimble of Philadelphia and presented by A. G. Perkin.<sup>2</sup>

TABLE XXX.—ANALYSES OF SUMACH

	Tannin.	Non-Tannin.	Insoluble.	Water.	Colour in Tintometer. ½ per cent. solution in 1 cm. cell.	
					Red.	Yellow.
<i>Rhus glabra</i> U.S.A.	24.6	16.5	51.8	7.1	1.3	3.2
„ <i>typhina</i> „	12.7	15.8	60.4	11.1	3.5	8.0
„ <i>aromatica</i> „	12.6	10.1	64.9	12.4	5.9	14.0
„ <i>cotonoides</i> „	20.4	12.6	58.3	13.7	3.3	7.3
„ <i>semialata</i> „	4.7	8.5	75.3	11.5	22.4	64.0
„ <i>metopium</i> „	8.2	13.0	68.5	10.3	—	—
„ <i>cotinus</i> , Italy	16.7	14.4	57.5	11.4	—	—
„ <i>coriaria</i> A. Sicily	27.1	16.9	47.7	8.3	0.8	3.0
„ „ B. „	26.7	14.8	50.5	8.0	0.9	2.5

*Lentiscus*.—One of the principal sophistications of Sicilian sumac is the addition of 20 to 60 per cent. of *Lentiscus* in powder, the latter being the leaves or petioles of *Pistacia lentiscus*, a shrub which grows more especially in Tunis, in Algeria, and in Corsica. This tannin principle contains not more than 10 to 15 per cent. of tannin, and does not give on leather the results furnished by Sicilian sumac. Tanners therefore would do well to make sure of the different qualities which are offered to them at prices which would indicate the extra-ventilated powdered quality (No. 1) or in leaf, but which in reality is a mixture "according to the formula" of Sumac *Lentiscus-Tamarix*.

*Tamarix*.—The leaves of this shrub, *Tamarix gallica*, *T. africana*, which grows in Tunis, in Algeria, and on the Medi-

<sup>1</sup> A. G. Perkin and A. E. Everest, *The Natural Organic Colouring Matters*, "Tannins," pp. 413-61.

<sup>2</sup> *Jour. Soc. Chem. Indt.*, 1902, 159.

terranean littoral, contain from 8 to 10 per cent. of tannin and are used to sophisticate Sicilian sumac.

According to Priestman<sup>1</sup> genuine sumac may be distinguished from the other leaves which are used as sophistications by the very hairy condition of both the upper and lower cuticles of the leaves, also by the nitric acid test of Lamb and Harrison.<sup>2</sup> The leaves of *Coriaria myrtifolia*, *Ailanthus glandulosa*, the common fig, *Ficus carica*, and the vine, *Vitis vinifera*, are also sometimes used as adulterants.

*Manufacture of Sumac Extracts.*—It may be stated at the outset that the plant and equipment of a sumac extract factory are similar to those used for the manufacture of oak extract, i.e. a battery of open vats and triple effect plant for the evaporation of the sumac liquors. There are two kinds of sumac extracts, cold extracted and hot extracted. The first called "blonde liquor" or purified 30° extract is the product of sumac leaves macerated in the cold or at about 30° C.; the second is the product of the hot macerated leaves. Moreover, there are found in commerce other inferior qualities from the maceration of a mixture of sumac lentiscus or tamarix, or of liquors concentrated by a second hot maceration of leaves, already cold macerated.

*Remarks on the Manufacture of Sumac Extracts.*—The oxygen of the air, aided by atmospheric ammonia, produces on certain vegetable liquors the following remarkable effects: (1) Conversion of white indigo into blue indigo; (2) colourless buckthorn extract changed into Lokao or Chinese green; (3) orceine, the colourless principle of *Archil lichens*, passes to the condition of orceine, a violet colouring principle which for seventy years has rendered great services in the dyeing of wool and silk. So we can justly ascribe to oxygen the same action on 5° to 6° B. extracts extracted from sumac in the open air. In fact, the first wash water cold drawn from the Sicilian sumac is colourless, the second is less so, and the degree of coloration is accentuated more and more up to the seventh washing, owing to the aeration produced by the action or emulsive power of the pump used to pass the liquors, which are pumped from below upwards and from one extractor to another, the latter seven times in succession. In order to ascertain the point at which this oxidation ceases, the authors spread 5° B. sumac extract in thin layers in the open air. After eight days it was completely black, passing through the following tints: yellow, rose, violet, blue, and green, indices of the formation of a large quantity of gallic acid. Ether extracted tannin, of prime purity, brought likewise to 5° B. and exposed

<sup>1</sup> *Jour. Soc. Chem. Indt.*, 1905, p. 231.

<sup>2</sup> *Jour. Soc. Dyers and Col.*, 1899, p. 60.



to the air in the same conditions, gave the same colour changes, but less rapidly, owing to the absence of the saccharine principles contained in sumac. It must therefore be concluded that tannins in a general way cannot support the action of the air without being influenced thereby, when they are diluted with a certain quantity of water, and that it is, therefore, of the greatest importance to prevent this contact during their extraction, their evaporation up to 25° and 30°, and even to the dry state. By pushing the evaporation to the dry condition they become unalterable, and can then be used as raw material for the manufacture of alcohol and ether-extracted tannins. For fine colours the loading of silk by tannins manufactured without access of air would perhaps give the ideal or colourless product. These considerations apply not only to the manufacture of sumac extracts but also to all the tannin extracts which require, in virtue of their composition, to be protected from the oxidation of the air as soon as they are in the condition of weak liquor. There is quite a large field for industrial experiments, the results of which would be of great value to the chemists of this industry, which is capable of numerous improvements.

*Cold Extract.*—Leaf sumac, according to the *modus operandi* of the authors, undergoes seven successive washings with cold water, after two hours' contact in each case. The following are the respective strengths: 1st liquor, 6° B.; 2nd, 4° B.; 3rd, 3° B.; 4th, 2.2° B.; 5th, 1.2° B.; 6th, 0.6° to 0.7° B.; 7th, 0.1° to 0.2° B.

As the leaves after maceration have to be fed into the gas generator furnaces in admixture with other waste, and as they absorb 275 per cent. of moisture, they are pressed in a mechanical press (100 to 150 kilogrammes) yielding 225 per cent. on the original leaf, as liquor of 0.8°, corresponding to 8 to 9 per cent. of 20° extract, or 3 to 4 per cent. of dry sumac extract (it requires about 270 kilogrammes of 20° extract to produce 100 kilogrammes of dry extract). The recovery is of course necessary to profitable working.

*Yield.*—As mentioned above, the yield in extract is a function of the quality of the sumac leaves treated; the yields, therefore, obtained by the authors were somewhat variable.

*Sicilian Sumac No. 1, Superior Quality.*—Yield of dry extract on leaves treated, 43 per cent.; of 25° extract, 92 per cent.; 20° extract, 110 per cent.; extraction done in the cold with recovery of the liquor contained in the marcs.

*Hot Extraction, 80° to 90° C., of 25 Tons of No. 1 Palermo Leaf Sumac.*—Yield of 25° extract, 78 per cent.; yield of 20° extract, 98 per cent.; in this yield the amount of extract obtained by the compression of the leaves after the seventh wash

ater, and which was used in the manufacture of the dry extract, has not been taken into account.

*Cold Extraction.*—Weight of sumac in powder treated, 100 kilogrammes; yield of 30° extract on powder, 55 per cent.; yield of 20° extract, 83 per cent.

*Other Yields.*—Hot extraction of No. 1 Sicilian extract, prior harvest. 123 kilogrammes of leaves yielded 120 kilogrammes of 25° extract; cold extraction of the same quality of sumac as the preceding, 162 kilogrammes of leaves yielded 120 kilogrammes of 25° extract. By pressing the leaves macerated in seven wash waters, and utilising the liquors, 0·8 per cent. dry extract was obtained.

*Qualities of Sumac Extract.*—Sumac extract for transportation is delivered commercially in the liquid state and at 30° B., there is, however, a certain quantity of dry sumac extract contained. As manufacturers of repute of this class of extracts, the authors would quote among English manufacturers: The British Dyewood Co., Ltd., Glasgow; The Yorkshire Dyeware Chemical Co., Ltd., Leeds, and McArthur & Co., Liverpool; in the United States, The American Tanning Material Corporation; the firm of Soc. Anon., Geigy & Co., of Bâle, who have been engaged in the manufacture of sumac and logwood extracts since 1856, and whose brands are universally appreciated, such as purified 30° sumac extract with 31·8 per cent. of tannin; in 30° with 32·4 per cent.; O 30° with 32 per cent.; B 30° with 25·5 per cent.; BO 30° with 23·7 per cent. These extracts are sold, according to quality, from 40 to 62 francs (1908). In France the authors mention the firms of Watrigant et Fils, of Arquettes-lez-Lille; Dubosc Frères, of Havre; Huillard et Fils, of Suresnes; Cie Francaise des Extraites Tinctoriaux et Connexes, Havre, and Veuve Paul Gondolo, Nantes, and in Italy, Ledoga S. A., Milan, late Lepetit, Dollfus and Gansser.

*Use in Tanning.*—Sumac extract is specially used to bleach leathers to be dyed rather than to tan them, because it tans too little; it is used especially for leathers intended for high-class boots, uppers, binding, and Morocco work. It is also adapted for dyeing white or pale-coloured silks.

*Gallo-sumac.*—Gallo-sumacs, made by the authors in large quantities, from mixtures in variable proportions of divi-divi, sumac, and chestnut, give good yields, and such extracts are appreciated by tanners on account of their high tannin content, which exceeds 32 per cent.

The sumac crop of Sicily amounted in 1914 to nearly 4000 tons. In 1915 it was rather above this figures, while the 1916 crop was well over 5000 tons. (U.S. Consular Report).

## CHAPTER VII

### KHAKI SUBSTITUTE FOR QUEBRACHO—ITS USE IN TANNING

THIS tanning material, recently placed on the market, would appear to come from Borneo (*vid* Singapore); it is extracted from a leaf and put on the market in a dry state. Khaki contains about 60 per cent. of tanning matter. It is rapid in its action and very astringent. It must, therefore, be used with moderation, preferably along with mild tannins, otherwise the pores of the leather may be contracted and tanning retarded. It yields a firm but soft leather, and less hollow than quebracho. Nourishing the leather by its assimilative capacity, it renders it waterproof. Khaki gives more weight, a thicker substance and a heavier leather than gambier, and in this respect it is much superior to quebracho, mangrove, mimosa, and other extracts used singly. It does not contain any resinous body, and is therefore unlike hemlock (spruce) and quebracho, which often are the cause of the spots or marblings to be seen on leather. It contains less than 1 per cent. of insoluble matter. In concentrated solution it does not separate as dry quebracho extract does. A strong liquor of khaki and hot water, or of khaki and a hot liquor consisting of other tanning materials, deposits naturally on cooling, but the deposit formed may be redissolved easily by treatment with hot water. This deposit is of a flocculent nature, having none of the resinous gluey properties so unpleasant in quebracho, mangroves, or the barks of mallet. Dry khaki extract is dissolved in the same way as chestnut (which see).

*Method of Application in Tanning.*—Khaki, being a tannin very soluble in water, may be employed in tanning, in admixture with other tannins, with which it gives good results, by proceeding as follows: Into a tan pit pump a myrobolam liquor, add 600 kilogrammes of gambier and 300 kilogrammes of khaki, dissolve by means of an open steam pipe at about 40° to 45° C., use this liquor afterwards either for the final tanning of leather or for the retanning of split leather. This formula is constantly used by English tanners, who obtain with this mixture first-class leathers. Another mixture consists of  $\frac{1}{2}$  khaki,  $\frac{1}{2}$  gambier,  $\frac{2}{3}$  myrobolam and oak bark, and drenching with

the preceding strong liquor. Khaki has also been used with success, by mixing it with chestnut extract in proportions varying from  $\frac{1}{10}$  to  $\frac{1}{2}$  of the tanning substances used, so as to mitigate the reddish colour of the khaki. Finally, some tanners have used the following mixture: Khaki  $\frac{1}{2}$ , chestnut extract  $\frac{1}{2}$ , to drench the semi-rapid tanning pits, and with liquors of 5° to 7° B. If the tanners use a system adopted in Germany, *i.e.* swell the leathers first in the pit with an organic acid, then dye them in the dye pits, and then lay them out in dry layers, it is advisable to add in the case of the first layers, to each fifty skins, four to six buckets of this strong khaki to the liquors used for drenching the said pits.

*Tanning of Sole Leather.*—Khaki may be used according to the following general formula for the manufacture of sole leather, which is followed in Germany and in Austria. The general system of tanning in Germany is to place the skins, after careful working in river water, to be dyed in a series of pits, the operation lasting several weeks, after which they are passed directly to the layer pits. These layers consist of bark and strong liquor, to which extracts are added to strengthen them. For this kind of tanning it is advisable in the first, the second, and perhaps in the third step, to dissolve the khaki in the liquor of the pits: 50 kilogrammes of khaki per 100 skins. The other system resembles more closely British tanning because khaki is used in the "handling" or in the powdering vats, at the rate of 50 kilogrammes (1 cwt.) per pit of sixty hides, dissolving it in the myrobolam liquor used for drenching the skins.

Finally, certain tanners use it with success along with oak bark, valonia, myrobolam, or chestnut extract, in proportions varying with the requirements and the exigencies of their methods, practice being the only guide as to procedure and proportions.

## CHAPTER VIII

### VARIOUS TANNING SUBSTANCES—THEIR MANUFACTURE AND USES

1. *Divi-Divi*—2. *Valonia*—3. *Chinese Galls*—4. *Myrobalam*—  
5. *Palmetto*—6. *Mimosa*—7. *Tara*—8. *Mangrove* (*Palétuvier*)  
—*R. Catechu* or *R. Gambier*

1. *Divi-Divi*.—This tanning substance is brought to market in the form of pods or siliquas of about 5 to 6 cm. long, fleshy reddish-yellow, bent in the form of an S, and containing hard, smooth, ovoid seeds; they are produced by the *Cæsalpinia coriaria*, which grows in the West Indies, Central America, Mexico, Venezuela, and Northern Brazil, and which also yields a bark used in tanning. The pods or siliquas contain about 30 to 45 per cent. of tannin, whilst the bark contains only 12 to 15 per cent. The tree has also been naturalised in Machas and Bombay Presidencies, and in the North-West Provinces, India. According to Dunstan the Bengal pod contains only 19·73 to 32·79 per cent. of tannin while American pods contain 30 to 50 per cent. The tannin is an ellagitannin probably accompanied by gallo-tannin (Perkin).

*Manufacture of Divi-Divi Extract*.—The divi-divi pods are exhausted by seven washings of two hours each at 90° C. (194° F.); then the first washing and the half of the second are evaporated *in vacuo* to a strength of 30° B. The following are the strength in degrees Baumé of the different liquors: First, 8·5°; second, 4·3°; third, 3°; fourth, 1·9°; fifth, 1·3°; sixth, 0·7°; seventh, 0·3°.

*Yield from a Lot of 50,000 Kilogrammes Treated (Maracabe and Rio-Aiche Quality)*.—100 kilogrammes of pods yielded 117 kilogrammes of 30° extract; 85 kilogrammes of pods yielded 100 kilogrammes of 30° extract; 168 kilogrammes of pods yielded 100 kilogrammes of dry extract. Divi-divi extract of 30° generally contains 30 to 33 per cent. of tannin, the dry extract 53 to 55 per cent. The extract, itself at 30°, being essentially fermentable, it is important to sterilise it by the addition of a small quantity of formic acid or mercuric iodide. The priming of the vats by the too intense fermentation developed in summer is thus avoided. Owing to its high yield of extract it will be seen

that this tanning material is of considerable value to the tanner, especially in tanning light pliant leather, decolorised extracts yielding very bright tints.

A sample of divi-divi pods from the Gold Coast, examined at the Imperial Institute, was found to be comparatively poor in tannin, containing 33.1 per cent. and was badly prepared. It is noted that the pods are richest in tannin when they have just arrived at maturity. They should then be collected and split longitudinally, the seeds removed and the husks dried as expeditiously as possible in the sun.<sup>1</sup>

There is a considerable trade in divi-divi pods in the Republic of Dominica, the annual exports from Monte Cristi in former years exceeding 2,000,000 lb., most of which was shipped to Hamburg, but this has been diverted during the last few years to New York where the demand is considerable. The production of this material is, however, diminishing owing to the damage which is done to the trees by a parasitic orchid which affects its yield of fruit and finally kills it.

Closely related to divi-divi is the *Cesalpinia digyna*, which is quite a common wild plant in Bengal, Burma, and Assam, the fruit being known in India as "tan" pods. These, according to T. A. Faust,<sup>2</sup> are almost round, about  $\frac{3}{4}$  inch diameter, dark brown in colour, and containing usually one or two large seeds. The pod cases are thin and contain sometimes as much as 60 per cent. of tannin. The leather produced by this tanning material is regarded as equal to that yielded by the best qualities of sumac.

Analyses of the pods yielded for the entire material, total extract 60.0, soluble solids 57.2, tannin 37.3, and non-tannin 20.0 per cent., while the pod cases contained total extract 63.4, soluble solids 61.0, tannin 42.6, and non-tannin 18.4 per cent. By grinding, the pods were separated into 46.1 per cent. of dust containing 46.6 per cent. of tannin, 16.1 per cent. of beans with 10.3 per cent. of tannin, and 37.7 per cent. of fibrous material with 18.6 per cent. of tannin.

Five samples of the pods examined at the Imperial Institute were found to contain from 53.82 to 59.89 per cent. of tannin, but one sample showed only 45.45 per cent.<sup>3</sup>

F. A. Blockey<sup>4</sup> obtained the following figures for a sample of this material :—

<sup>1</sup> *Bull. Imp. Inst.*, 1913, p. 401.

<sup>2</sup> *Jour. Amer. Leather Chem. Assoc.*, 1912, p. 154.

<sup>3</sup> *Bull. Imp. Inst.*, 1912, p. 219.

<sup>4</sup> *Jour. Soc. Chem. Indt.*, 1902, p. 159.

TABLE XXXI.—ANALYSES OF DIVI-DIVI

Material.	Tannin.	Non-tannins.	Insoluble.	Water.
<i>Caesalpinia digyna</i> —				
Pods, shell cases only.	43.9	20.4	25.3	10.4
Pods, including nuts.	23.5	20.1	46.5	9.9

2. *Valonia*.—Valonias are the scaly acorn cupules of the *Quercus Ægilops* (Turkey Oak), a tree common to the Greek Archipelago, Asia Minor, Greece, and Palestine. The product may possibly be obtained from other species, e.g. *Q. coccifera*, *Q. Græca*, *Q. macrolepis*, and *Q. rugerii*. German, Austrian, Italian, and especially British tanneries consume large quantities of it. Valonia is mixed with oak bark for the tanning of sole leather in the two last powders; the resultant leather being more water-resistant than that tanned by oak bark alone. It is in fact one of the best tanning agents at present on the market, and British tanners make excellent use of it, if one can judge from the leathers imported into France. The chief market is Smyrna, which exports all the known varieties: Caramania 1a and 2a, Camatina, bons refusos, English 2a without trynacks, uso-English, unacqua, trynacks trillos 2a or 1a sifted, Greek dragoman; the price of these different qualities varying from 16 to 27 francs c.i.f. Havre, Dunkirk, Antwerp (1908). As the tannin content of valonias may vary from 15 to 35 per cent. or even more, according to quality, source, etc., it is very important when buying to determine their tannin content, the more so as the percentage of extractive matter is also very variable.

*Manufacture of Valonia Extract*.—The authors had occasion to treat 10 tons of a lot of mixed valonias which received seven wash waters at 95° C. (203° F.), each of one and a half hours' duration. Strength of the respective liquors: (1) 5.3° B.; (2) 3° B.; (3) 1.2° B.; (4) 0.8° B.; (5) 0.5° B.; (6) 0.2° B.; (7) 0.1° B. The average strength of the liquors was 4°. After cooling, decolorisation and evaporation *in vacuo*, they yielded a 25° extract, the tannin content of which was 26 per cent. Yield: 117 kilogrammes of cupules produced 100 kilogrammes of 25° extract, or 85 per cent. of the weight of the valonia treated.

Smyrna valonia contains up to 40 per cent. of tannin, Candia valonia 41 per cent., and Greek valonia 19 to 30 per cent. The tannin is a mixture of ellagitannin and gallotannin (Perkin and Everest). The following analyses by J. Gordon Parker and F. A. Blockey of valonias represent the composition of the whole material and also that of the cup and the beard.

TABLE XXXII.—ANALYSES OF VALONIA

	Tannin.	Non-tannins.	Insoluble.	Water.	Tintometer. $\frac{1}{2}$ per cent. solution in 1 cm. cell.	
					Red.	Yellow.
Smyrna valonia	32.43	12.50	43.07	12.00	1.6	5.6
" " cup	30.99	12.79	44.12	12.00	1.7	4.6
" " beard	43.61	14.45	29.93	12.00	1.2	4.1
Greek valonia	32.07	12.96	42.97	12.00	1.5	5.0
" " cup	27.37	12.92	47.71	12.00	2.0	6.7
" " beard	41.03	13.96	33.01	12.00	1.3	4.4

TABLE XXXIII.—IMPORTS OF VALONIA

Valonia.	Imports into Great Britain. Tons.				
	1911.	1912.	1913.	1914.	1915.
Liverpool . . .	3,310	3,920	3,438	4,294	5,602
London . . .	2,348	4,128	3,740	2,985	
Bristol . . .	1,109	1,912	2,452	2,593	
Other outports . .	5,633	4,435	7,675	8,200	
	12,400	14,395	17,305	18,072	7,118

3. *Galls*.—The gall nuts used in tanning are a morbid secretion formed on small oak trees (*Quercus lusitanica*), which is indigenous to Greece, Cyprus, Syria, and Asia Minor. By the puncture of a winged insect, *Cynips gallæ-tinctoria*, a spherical gall nut enclosing the larva of the insect, is formed on the tree. When the insect arrives at maturity it bores its way through the gall nut and escapes, leaving a visible perforation. The highest percentage of tannin, *i.e.* 50 to 60 per cent., is found in the nuts before the insect escapes, these being therefore unperforated, heavy and of an olive-green colour. They are known in the trade as blue, black, or true nuts, while the perforated pale coloured and larger galls are very much inferior. The best galls come from Aleppo, and other varieties from Smyrna, Austria, and Hungary.

Chinese galls are quite a different product formed by the puncture of an insect, *Aphis Chinensis* on a species of sumac (*Rhus semialata*), which grows in Northern India, China, and Japan, attaining to a height of 30 to 40 feet. These galls are larger than oak galls, more irregular in shape, hollow, with very thin walls, and are exceedingly rich in tannin which may amount to as much as 60 or even 70 per cent.



Chinese galls are usually employed in the manufacture of pure tannic acid. Treated in the same way as divi-divi or valonia they yield 125 to 128 per cent. of 30° extract, *i.e.* 78 kilogrammes of Chinese galls yield 100 kilogrammes of 30° extract.

A specimen of galls ("Gool-i-pista") from *Pistacia vera*, India, examined by F. A. Blockey yielded: Tannin 30.1, non-tannins 17.8, insoluble 42.4, and water 9.7 per cent.

4. *Myrobalam* or *Myrobalans*.—This tanning agent comes from India as rounded, greyish-black nuts, collected from several species of large trees (*Terminalia*) and containing, according to source and year, 25 to 35 per cent. of tannin. The best kind is the chebolic myrobalams from the "hirda or harea" tree, (*Terminalia chebula*) which grows in China and the East Indies. The best varieties contain 30 to 40 per cent. of tannin. The tannin, which is a gallotannin (partly chebulinic acid), is contained entirely in the pulp of the fruit, the hard stone being free from it (Perkin and Everest). Emblic myrobalams from the "Aowla" or "Awla" tree (*Phyllanthus emblica*) and Beleric myrobalams from *Terminalia belerica* are inferior to the chebolic variety.<sup>1</sup>

The following are analyses of the different commercial grades of myrobalams, by Dr. J. Gordon Parker and F. A. Blockey:—

TABLE XXXIV.—ANALYSES OF MYROBALAMS

Designation.	Tannin.	Non-tannins.	Insoluble.	Water.	Tintometer. ½ per cent. solution in 1 cm. cell.		
					Red.	Yellow.	Black.
Picked Bhimley . .	33.0	13.1	41.7	12.0	0.8	2.5	—
Bhimley 1 . . .	38.4	16.1	33.5	12.0	0.3	1.8	—
Bhimley 2 . . .	35.2	14.2	38.6	12.0	1.0	5.1	—
Picked Rajpore . .	32.2	13.0	42.8	12.0	1.1	3.0	—
Rajpore 1 . . .	35.4	12.1	40.5	12.0	0.9	4.0	0.1
Rajpore 2 . . .	27.6	12.7	47.7	12.0	2.5	7.4	—
Picked Jubbulpore	28.9	12.7	46.4	12.0	0.8	2.2	—
Jubbulpore 1 . .	36.5	14.4	37.1	12.0	0.8	3.4	—
Jubbulpore 2 . .	27.3	14.1	46.6	12.0	1.3	5.9	—
Vingorlas . . .	31.5	9.5	47.0	12.0	1.2	3.0	—
Fair Coast Madras	34.8	15.4	37.8	12.0	1.2	3.9	—

In the market Bhimlies fetch the highest price, Jubbulporees and Rajpores following next in order.

The authors had occasion to treat some tons of Jubbulpore I.-II. by seven washings at 90° to 95° C. (= 194° to 203° F.).

<sup>1</sup> Sir George Watt, *Commercial Guide to the Forest Economic Products of India*, 1912, p. 133.

The following are the results obtained : Yield of 20° extract per cent. of myrobalam treated = 76 per cent. ; of 25° extract = 60 per cent. Weight of myrobalam required to produce 100 kilogrammes of 20° extract = 145 kilogrammes. The liquor obtained, which showed a strength of 3·7°, decants easily and rapidly ; evaporated at 65 cm. vacuum, it yielded a very fluid extract of a yellow colour, useful in tanning goat skins a brilliant yellow and endowed with great pliancy. Moreover, it is a tannin of universal good repute which mixes very well with bark liquor or chestnut extract. The chief makers of French and foreign myrobalam extract are Compagnie Française des Extraits Tannantes et Colorantes, Watrigant et Fils, etc., see also for other makers P.

A solid extract is made in India by the East Indian Tanning Extract Co., Ltd., at Raneegunge, which, according to Sir George Watt (1912), manufactured and exported 1000 tons annually.

F. A. Blockey<sup>1</sup> has also analysed the products from three species of *Terminalia*, the results being given below :—

TABLE XXXV.—ANALYSES OF MYROBALAMS

	Tannin.	Non-tannins.	Insoluble.	Water.
<i>Terminalia tomentosa</i> nuts	10·6	26·8	51·9	10·7
<i>Terminalia bellerica</i> nuts .	8·3	16·6	65·7	9·4
<i>Terminalia oliveri</i> bark .	31·1	10·2	48·4	10·3
<i>Terminalia oliveri</i> leaves .	14·4	12·2	64·5	8·9

The exports of myrobalams from India amounted to :—

TABLE XXXVI.—EXPORTS OF MYROBALAMS FROM INDIA

	Weight. Cwts.	Value. Rupees.
1900-1	945,648	31,68,173
1901-2	1,085,174	35,63,652
1902-3	1,157,650	37,72,255
1903-4	1,229,609	42,10,288
1904-5	1,187,585	42,59,063
1905-6	1,206,398	44,60,676
1906-7	1,162,219	43,97,591

5. *Palmetto Extract*.—This tanning agent is extracted from the roots of the *Sabal palmetto* (*S. surrulata*), which grows on the sandy maritime soils of Florida, and the extract is manufactured by the Florida Extract Company, Titusville, Florida. The chief use of palmetto extract is as a gambier substitute.

<sup>1</sup> *Jour. Soc. Chem. Indt.*, 1902, p. 159.

The following are the properties which give palmetto an advantage over gambier: "It tans more rapidly, gives a greater weight, produces stronger leather by causing it to swell, and moreover the leather may undergo a higher temperature in varnishing". Palmetto extract, or new tanning agent, seems to be destined to play a very important part in the tanning industry. Precise data as well as instructions on the method of applying it to the most different kinds of leather now follow, based on the numerous experiments and laborious researches of Prof. Kohnstein of the leather factory of Pfistervogel, Milwaukee. Palmetto extract is sold in American tanneries by the waggon-load, and its consumption increases in proportion as it is adopted in actual practice and that the practitioner recognises its valuable qualities. In the beginning the high figures for the percentage of non-tannins, determined in the laboratory, could not be overlooked, and moreover also all sorts of difficulties combined to throw discredit on the use of palmetto extract. First of all, the difficult solubility of the extract in cold water was against it, and also the fact that the extract seemed to become darker when exposed to the air, and especially to light. In spite of these unfavourable observations, demonstrated both in the laboratory and in the works, Kohnstein did not abandon his researches but continued his experiments with this new product. The experience acquired in the manufacture of the extract and in tanning showed that the same difficulties had to be overcome as in the production of tanning extract from pine and oak wood and quebracho extract. In fact, with the best bark and the finest calf skin, very bad leather may be produced if the operator has no knowledge of tanning processes. To tan by means of palmetto extract, it requires as much experience as in working with the best oak bark. Thanks to laboratory researches and to the experience acquired in the factories themselves, it is now possible to supply the chemist as well as the practitioner with some valuable advice concerning the application of this extract and its judicious use. The preliminary treatment of the leather must also be explained, because it is very important in tanning with palmetto extract. This treatment depends on the characteristic properties of leather. The Florida Extract Company have lately sent out samples of extract of the following average chemical composition: Density, 30° B.: water, 52.94; ash, 11.09; tannin, 25.96; organic substances other than tannin, 10.31 per cent. The extract being soluble in cold water at a temperature of 65° F., yielding a bright red coloured solution.

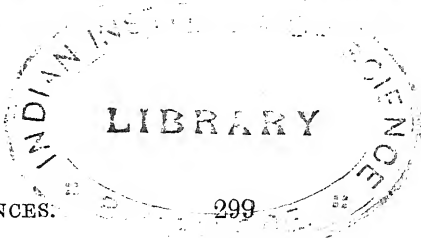
In analysing palmetto extract it has been observed that the hide powder is dissolved to some extent by the inorganic substances of the extract, which are to some extent alkaline in their nature. Attention has first of all to be drawn to a point already

demonstrated in previous publications, *viz.*, that palmetto extract contains natural alkaline chlorides and bromides. This is shown in the laboratory researches of the State of Florida of June 17, 1898, in which are published the analyses of palmetto root by the State chemist, W. A. Rawls, from which it will be seen why chemists found so much non-tannins, this is due to the fact that the hide powder dissolved causes a very appreciable increase in the apparent non-tannins and a decrease in the tannin. This error was pointed out in 1897, at the Congress of Leather Chemists in London. The same error occurs with extract to which borax is added, either as an antiseptic or to accelerate the solubility in cold water. If a certain quantity of palmetto extract be ignited, and the residual ash dissolved in water and filtered through hide powder, working on weighed quantities, the chemist will be able to acknowledge the correctness of these remarks, and he can then afterwards avoid this error. Palmetto extract is chiefly intended as a substitute for gambier or for use in admixture therewith. The following are in a few words its advantages: "Palmetto extract gives a considerable weight, tans rapidly and renders the leather thicker by causing it to swell, finally it stands heat well during greasing in the cask, during varnishing and the drying of the varnish in the stove (that is, during japanning)". These valuable properties have led to palmetto extract being used for the most diverse kinds of leather. The dark colour of the leather may be explained and the inconvenience incidental thereto be remedied, chiefly by drying, when it has been exposed for some time to broad daylight. The practical tanner knows that tannin solutions containing alkaline salts easily absorb oxygen and become darker, but if the skins be treated with a little soap or grease the alkali is neutralised by the grease, and the good effect of a fat liquor is at the same time obtained on the leather, producing a material of excellent quality and very fine colour. In retanning chrome leather, such salts are very useful since they neutralise the traces of acid remaining in the leather, and by forming, in combination with the tannin of palmetto, a superb mordant for leathers to be dyed black with iron salts or with aniline dyes. Silk, woollen and cotton dyers have not been slow to appreciate in their turn the value of this mordant, palmetto extract being free from resin and fat, and penetrating easily into the fibre. In retanning chrome leather with palmetto extract excellent results are obtained, which it would be difficult to produce with other tannins; the grain remains soft, does not become rough nor slack, and produces a very soft texture of excellent appearance.

*Tanning of Calf Skins and Kips.*—The crude green salted skins are first passed into fresh water, twice renewed, then the

third day they are broken over by hand or machine and put into the lime vats. The first lime is left till it gets "killed," and the skins are left in it a day and covered each day with a fresh layer of lime until they pass the fifth day in a fresh lime vat. In the case of fresh skins, for every 3000 lb. of raw skins 150 lb. of lime and 8 lb. of arsenic are taken. To strengthen the succeeding limes, each time the skins are turned, 70 lb. of fresh lime and 4 lb. of arsenic are added. The sixth day the skins are unhaired and put into milk of lime for twenty-four hours. For 3000 lb. of raw skins there are taken for this solution 70 lb. of pure lime dissolved in water. After this operation the skins are re-paired, the heads are split, washed, and finally assorted.

*For a chrome mixture* the skins require a bran drench; for tanning by the "Palmetto Extract Method," or for mixtures with other vegetable tanning agents, a bating of pigeons' dung is recommended. For "glazed kid," goat, lamb and sheep skins, intended to be dyed, so as to prepare them for tanning by palmetto extract and chrome, dogs' dung is to be used. After paring the skins and smoothing the grain they are ready for tanning. They are then steeped in a palmetto liquor of 8° Barkometer and removed in half an hour. They are then tanned in a fulling machine by means of palmetto extract of 30° B. (51° Twaddle), heated up to 35° C. (95° F.). For 700 lb., the weight being taken after the skins leave the beam-house, 500 lb. (one barrel) of extract is run into the vat. In order to prevent the skins from twisting and getting entangled they must be inspected from time to time, and the fulling machines adjusted in such a way that the paddles make the same number of rotations in both directions. After having been continuously mixed for five or six hours the skin is well tanned, even in the strongest places of the nape of the neck and the cheeks, without drawing or roughening the grain. The skins are then rinsed in a light liquor, in which the skins are dyed and pressed. They should then be passed into a weak palmetto liquor of 8° Barkometer, and retanned one hour in a strong solution, in the fulling machine. When taken out of the fulling machine they are washed in lukewarm water, this liquor being used as the dyeing liquor. When the skins have been washed and pressed, they are thrown directly into a fulling machine containing heavy liquor. The fulling machine is heated by steam to a temperature of 140° F. For 440 lb. of pressed leather 5 lb. of soap, 4 litres (1 gallon) of sod oil heated in a cask half filled with water to a temperature of 120° F., are used, treating the mass in the fulling machine for half an hour. The door is then opened and water run on to the skins to wash them, after which they are hung up to dry. The grain of the leather may easily be protected if the skins are to be dyed. So if the dry skins have accumulated a few days,



they may be joined to the different kinds of leather, and after a preliminary treatment with Sicilian sumac, they will be as good for varnished and dyed leather as gambier tanned leather.

*Tanning of Cow-hide Sole Leather, Harness Leather for Saddle-girths, Machine Bands, etc.*—The well-cleansed and washed skins are broken and put into lime vats strongly blended with sodium sulphide. For 3000 lb. of raw hides, 210 lb. of lime and 20 lb. of sodium sulphide are used, and 75 lb. of lime and 10 lb. of sodium sulphide are used later to strengthen the vat. After having been in lime for five days, the skins are unhaired by the unhairing machine, smaded, after being washed with cold water they are mordanted with cold muriatic acid—18 lb. acid per 3000 lb. of hides; then they are treated with a bath of pigeons' dung for two hours, with constant agitation. The skins are afterwards scraped and hung in vats filled with dye of 12° density, which may be brought to 20°. With the first palmetto bath it is advisable to leave spaces between the skins when suspending them, so as to facilitate uniformity in the dyeing of the grain. The sixth day the hides are lifted with the poles, and laid flat in palmetto extract of 30° B., turning them twice the first day. In order that no loss nor leakage of extract may occur, it is advisable to place the hides on sloping boards. The skins are tanned in four days: it will then be seen that the extract, without any motion, has penetrated even the densest parts on the top. The hides are slightly rinsed in weak palmetto extract, exposed to the air and fleshed. After fleshing, the hides are re-tanned with weak palmetto liquor, and finally fullled in a fulling vat of 30° B. for six hours. To obtain a bright yellow effect with this kind of leather on drying, it is advisable to use the fat liquor called "sod oil" (*Moellon dégras*) described above. Moreover, palmetto extract is well adapted for tanning split leather, for the production of heavy leather for soles, in combination with other tannins, such as valonia and oak. Finally, combined with gambier it is an excellent medium for softening leather, and imparting to it a greater capacity to resist heat.

*Chrome Tanning with Palmetto.*—No other tanning agent is so well adapted for use in conjunction with chrome compounds as palmetto extract. The Florida Extract Company of Titusville were the first to discover this peculiarity, and it is to them that palmetto extract on a chrome mordant owes its reputation for woollen and cotton dyeing. For hides tanned in two chrome baths, it is advisable to re-tan in a palmetto extract liquor. For 300 lb. of pressed chrome hides 23 lb. of palmetto extract, with 1 pint of glycerine, dissolved in a cask of water are used. Chromed leather treated in this way is exceedingly well adapted for being dyed, the grain becomes firmer, and is not detached

on rubbing. Aniline dyes, logwood, or other dyewoods, such as fustic or redwood, are more fast to light, etc., do not become dirty, and are easily glazed. This leather is also better fitted for taking sod oil (*Moellon degres*); it preserves its silky grain—for which reason it is the best material to use for dyed chrome leather for gloves. Hides which are to be tanned after the chrome bath, may be treated similarly; however, the chrome bath may follow the tanning with palmetto. Above all, palmetto extract is distinguished by the fact, that although containing 28 per cent. of tannin it is very liquid, penetrates the main body of the leather very energetically, in spite of its concentration, *i.e.* 30° B., and is consequently well fitted for tanning by Durio's process.

*Another Method of Tanning by Palmetto Extract. Tanning of Goat, Sheep, and Calf Skins, with that Extract according to the "Shoe and Leather Reporter".*—Lately, and especially in America, tanning with palmetto extract has assumed enormous proportions, because it yields a very good soft and full upper leather. Recently it has also been used for goat, sheep, and calf skins, the process being as follows. First the skins are cleansed with special care and attention. It is especially necessary to use arsenic depilatories, and it is important that the skins should be laid perfectly soft and in good order in the depilatory. These are preferable to the ordinary depilatory, because a better grain and a firmer texture are imparted to the skin, precisely the qualities required in goat and sheep-skin leather. An old depilatory is used at the commencement, in which the skins are laid for some days, then they are passed through depilatories of gradually increasing strength, one after the other, until the unhairing is complete. It is not believed to be desirable to use lime liquors in the beginning, but the skins may be placed, after five or six days, in quite fresh lime, after passing through several depilatories. For the preparation of the latter, for 1 ton of skins 1 cwt. of lime and 6½ lb. of arsenic are used. The third day the skins are taken out and unhaired, and if a very fine skin be desired they are replaced in fresh lime for twenty-four hours, after which the skins are smaded and are ready for tanning.

*Branning.*—The skins are placed in a bran steep, good results being obtained as follows. Half a ton of bran is taken for 400 heavy or 450 light skins, and run into a vat with enough water to form a greasy paste which is soured, taking about forty-eight hours. There is added to this "branning" medium about 1 litre to 1½ litres of sulphuric acid, and 93 to 95 kilogrammes (204.6 to 210 lb.) of pure salt, so as to get a density of 58°. The skins are stirred in this liquor for three to five hours, the time depending on the depilatory and the amount of lime which



they contain; they are then withdrawn. This maceration renders the skins pliant, and gives them a fine grain. The skins are prepared for tanning by gentle washing in lukewarm water, working them softly on the grain.

*Tanning.*—To feed them to the end palmetto extract is used. The skins are first weighed, if they come from the previous workshop in good condition. They are then laid in a weak bark liquor of 8° Barkometer strength in which they are stirred for about thirty minutes. They are then put with constant stirring into a palmetto liquor of 35° Barkometer heated to about 47° C. (122.6° F.). A liquor is prepared for 100 skins containing about 65 kilogrammes (143 lb.) of palmetto extract and the necessary water. Tanning is complete in five to six hours. It is not necessary that light skins be re-tanned, but it is better to tan heavy skins once more after cleaning and stretching, and in that case, fulling the skins a second time about an hour in a weak liquor. When tanning is complete the skins are taken out of the vat and washed perfectly in lukewarm water; they are pressed and treated with sod oil (fat liquor).

*Finishing.*—The leather may be finished in two different ways: it may be passed into the "fat liquor" (sod oil), dried, coloured, finished, or it may be oiled in the ordinary way in the fulling mill, then dried, again oiled, dyed, and finished. The first method is better than the second, as the leather has a better appearance and labour is saved. The method of preparing the "fat liquor" (sod oil) is described later. The skins are well rubbed with this lubricant and fulled for half an hour in the fulling machine; they are then laid out to dry. The dried skins are run in lukewarm water and coloured blue on the flesh side with crystallised logwood extract and flesh stain D, and on the grain side with leather black; they are oiled both sides, again dried, stretched, and finished in the ordinary way. The different sorts of Levant Ink (inks to be applied before finishing) may also be used according to whether black or pale leather is to be made.

*Feeding for Use in the Churn. Fat Liquor P.*—For 100 kilogrammes of skins take 2½ to 4 kilogrammes of this composition. Soft skins require the minimum, hard skins the maximum quantity. Weigh the requisite quantity of fat liquor and place it in the churn with half the total water to be used. Do not boil, but heat and stir until solution is complete. Then add the other half of the water to bring the liquid to the proper temperature for feeding. Then proceed as usual.

*Oil Emulsion to be Rubbed into the Skins. Fat Liquor A.*—Take 2 kilogrammes of this emulsion, heat it to boiling, add 1 litre of water; then rub this composition into the skin with a woollen rag, at a temperature of about 60° C. (140° F.).



When the skins are treated, instead of placing them grain upon grain, they must be placed flesh upon grain. If the emulsion be heated by a steam jet, it will not be necessary to add the above litre of water, because the condensed steam will suffice. The skins when treated are taken to be dried, then when dried they are left in a heap for four to seven days, then moistened and passed through the staking machine and finally placed on the straker. They are then ready for drenching before finishing.

6. *Mimosa*.—These (wattle) barks, which come from Australia, are the product of different species of *Acacia*, such as *A pycnantha cyanophylla*, *leiophylla*, *mollissima*, etc. They have been cultivated for some years both in Tunis and Algeria with good results and even in the south of France, where their culture might be developed with success, the mimosa being a hardy shrub which requires but little care and is very productive, as certain mimosas shoot continuously from the stump after being felled, and a tree decorticated when six years old may yield 20 lb. of bark. Moreover, a hectare of mimosas will yield according to the quality and nature of the tree and the climate in which it grows, 4 to 5 tons of bark per hectare (32 to 40 cwt. per acre). The mimosa bark of Natal, one of the most highly prized, contains 34 to 36 per cent. of tannin, and will yield 110 to 112 kilogrammes of 25° extract per 100 of bark, say 90 kilogrammes of bark to produce 100 kilogrammes of 25° mimosa extract. With mixed qualities the authors obtained 103 per cent. in one case, and 96 per cent. of 25° extract in the treatment of bark of Algerian origin. This bark yields on maceration liquors which easily reach 5° to 6° B., which, concentrated in a vacuum of 65 cm., yield an extract readily soluble in cold water, without any decolorisation or clarification. It is thus an excellent tanning material for the manufacturing of tannin extracts, the more so as it yields in practice fine coloured leather of superior quality. The erection of mimosa extract factories in Australia and even in Algeria will give rise to a series of interesting commercial developments for some time to come. The following are the yields from Hyères (Var) mimosa bark treated like the foregoing: Yield per cent. of bark of 20° extract = 80 per cent. ; of 25° extract = 64 per cent. Quantity of bark required to produce 100 kilogrammes 25° extract = 156 kilogrammes. The authors found this bark to yield on analysis 29 per cent. of tannin and the corresponding 25° extract 32 per cent. of tanning matter. These yields may be taken as commercially possible as the experiments were made on half a ton of bark. It will thus be seen how desirable it is to form plantations of, and cultivate, this genus, the yield of bark per hectare of mimosa and that of the extract per 100 kilogrammes treated being so good. As a working basis, 2000 to 3000 hectares (say 5000 to 7500 acres) planted with

mimosa would suffice to supply a factory treating 25 tons which would produce 15 tons of 25° extract. Extract makers will soon be more and more compelled by force of circumstances to use tropical tanning material either by treating them on the spot, or by acclimatising them in tropical colonies, for capital is best utilised in the development of prosperous industries, and it may be justly said that the tannin industry is one of the most lucrative. The price of mimosa bark varies according to its source between 18 and 27 francs per 100 kilogrammes for good qualities c.i.f. Havre or Marseilles (7s. to 10s. 6d. per cwt, 1908).

There are a very large number of species of wattles growing in Australia; the barks of some being comparatively rich in tannin, the latter have been exploited to the fullest degree and are now depleted to such an extent that the production is not equal to the demand which has to be made good by imports from Natal. The barks used mostly in Australia are those of the golden wattle (*Acacia pycnantha*) of South Australia and the black or green wattle (*A. decurrens*) and varieties of the same.

The following figures show the content of tannin in the bark of various species of wattle:—

TABLE XXXVII.—TANNIN CONTENT IN WATTLE BARKS

	Per cent.
<i>Acacia implexa</i> (black wattle)	over 20
„ <i>harpophylla</i> (brigalow, W. Australia)	16
„ <i>decurrens</i> (common wattle)	8 to 38
„ „ var. <i>molissima</i>	8 to 33
„ <i>penninervis</i> (South Queensland)	17.9
„ <i>saligna</i> (South-West Australia)	30 nearly
„ <i>pycnantha</i> (golden wattle)	25 to 38 (dry)

The following analyses of Australian wattle barks are by F. Austyn Blockey:—<sup>1</sup>

TABLE XXXVIII.—ANALYSES OF WATTLE BARKS

Botanical Name.	Local Name.	Tannin.	Non-tannins.	Insoluble.	Water.
<i>Acacia pycnantha</i>	Golden wattle				
„ „	No. 1, special	49.5	9.4	29.9	11.2
„ „	Golden wattle				
„ „	No. 2, ordinary	40.2	9.0	35.6	11.2
<i>Acacia decurrens</i>	Sydney green				
var. <i>normalis</i>	wattle	41.4	7.9	39.2	11.5
<i>Acacia decurrens</i>					
var. <i>leichardtii</i>	Green wattle	38.5	9.1	41.4	11.0
<i>Acacia decurrens</i>					
var. <i>pauciglandulosa</i>	Green wattle	36.1	7.8	44.5	11.6
<i>Acacia decurrens</i>					
var. <i>molissima</i>	Black wattle	38.3	4.4	46.2	11.1
<i>Acacia penninervis</i>	Hickory bark	37.7	5.2	46.1	11.0
„ <i>binervata</i>	Black wattle	30.2	6.7	52.0	11.1
„ <i>dealbata</i>	Silver wattle	12.7	4.3	71.9	11.6
<i>Acacia Smithii</i>	Lilly pilly	10.7	16.1	62.2	11.0

<sup>1</sup> Jour. Soc. Chem. Indt., 1902, p. 159.

The wattle has done extremely well in South Africa, especially in Natal where it has been planted from Australian seed, and the industry has now reached considerable proportions, so that with the cheap native labour available it seems impossible for Australia to offer any serious competition. The wattle trees arrive at maturity in about six years, and will then be about 6 or 8 inches in diameter. At about this period a cut is made in the bark which is then peeled off and hung up on poles in a shed to dry, losing in the process 30 to 40 per cent. A mature tree of about 8 inches diameter will yield 100 to 110 lb. weight of dry bark, equal to a production from 500 to 600 trees of about 4 to 4½ tons to the acre.

The species grown in South Africa are *Acacia decurrens*, or black wattle, *A. pycnantha*, and *A. molissima*.

According to the *Bulletin of the Imperial Institute*, 1916, p. 599, the production of wattle bark in Natal in 1913 was 1,300,000 cwt. corresponding to 2,350,000 cwt. of green undried bark. Out of this total 811,000 cwt. valued at £325,000 was shipped to the United Kingdom. The trade in the bark has increased enormously in the last few years, but naturally there was a set back during the period of the war. One factory for the manufacture of extract was erected and two others were under construction. These, when working to the full capacity, will be capable of dealing with two-thirds of the total production. It is also mentioned that several patents have been taken out for the manufacture of extract by new processes. In one of these processes the bark is crushed between bronze rollers while it is subjected to the action of a stream of water which dissolves the tannin as it is pressed out of the cells. In the other process the bark is first cut into chips which are similarly crushed and afterwards extracted in the ordinary way in large vats. This process, however, is not a new one since it was described as far back as 1882 (see p. 308).

There are two firms in South Africa preparing wattle (mimosa) extract, these being the Natal Tanning Extract Co., and the Natal Wattle Products Co., Ltd.

The following table shows the exports and value of wattle bark from the Union of South Africa, and also the price of chopped bark in London :—

TABLE XXXIX.—EXPORTS OF WATTLE BARK FROM SOUTH AFRICA

Years.	Tons.	Value.	Price per Ton.
		£	£ s. d.
1896	3,378	16,450	9 7 0
1898	9,429	30,929	8 4 0
1900	9,800	46,479	8 15 0
1902	15,537	74,554	8 5 0
1904	14,124	92,911	7 18 0
1905	15,636	—	—
1906	14,828	89,836	8 5 0
1907	24,321	—	—
1908	24,849	133,509	7 18 0
1909	36,771	—	—
1910	41,344	219,433	8 3 0
1911	49,645	—	—
1912	52,766	283,160	7 1 0
1913	65,042	309,268	7 1 0
1914	58,132	286,399	7 11 0

The following shipments of wattle bark and other tanning barks were made from Australia in 1911 and 1912:—

TABLE XL.—EXPORTS OF WATTLE BARK FROM AUSTRALIA

	1911.		1912.	
	Tons.	Value.	Tons.	Value.
		£		£
To Germany . .	7,424	58,516	2,500	20,079
„ Belgium . .	1,455	11,267	2,009	15,106
„ New Zealand .	3,284	27,928	3,166	28,830
„ other countries .	455	3,464	217	1,707
Total . .	12,618	101,175	7,892	65,722

Black wattle is now cultivated on an extensive scale in East Africa, according to the Chairman of the Wattle Grower's Association over 12,000 trees having been planted in that protectorate. Exportation of the bark commenced in 1911-12 by the shipment of the first ten tons. The annual output, however, at present is probably upwards of 7000 tons. The thick bark has been found to contain more tannin than the thin bark, but in several average samples examined at the Imperial Institute the percentage of tannin was found to vary from 29·4 to 43·6, only three samples containing less than 35 per cent.<sup>1</sup>

7. *Babul Pods*.—The fruit of the babul tree (*Acacia ara-*

<sup>1</sup> *Bull. Imp. Inst.*, 1913, p. 401.

*bica*) are used as a tanning material in India. They are fairly rich in tannin but are not exported. The tree also grows in the Sudan and Northern Nigeria. Samples from the Sudan, examined at the Imperial Institute, were found to contain 30 per cent. of tannin, but the powder obtained by lightly grinding and sifting the material contained 55 to 61 per cent. of tannin. The pods from Nigeria yielded on analysis 26.7 per cent. of tannin.

In India the bark of the babul tree is also used in tanning, and in the Cawnpore factories as much as 500,000 maunds of it are annually consumed (Sir George Watt).

8. *Algarobilla*.—The pods of the carob tree of Chili, known usually as algarobilla or algaroba (*Caesalpinia brevifolia*), are extremely rich in tannin, containing on the average 45 per cent. These pods are broad, flat, and thin and containing small pale-brown seeds. The colour of the pods is pale cream to pink and they are extremely brittle, the tannin breaking away from the pod in small flakes leaving only a skeleton or framework behind. The tannin is probably an ellagitannin, and this material is very suitable for the preparation of white or pale-coloured leathers.

9. *Cassia Bark*. *Tanner's Cassia*, *Tarwai* or *Tarwad*.—Tarwar bark, the product of *Cassia auriculata* of Central and of Southern India, is used in India as a tanning agent. In young plants Hooper<sup>1</sup> found 22.35 per cent. of extract with 11.92 per cent. of tannin, and in old plants 29.0 per cent. of extract and 20.12 per cent. of tannin. Professor Hummel found 20.5 per cent. of tannin and Mr. Leather 15.5 per cent.<sup>2</sup> It is used for tanning purposes very extensively in Bombay and district, but is not exported to Europe. Samples of the bark from several districts of Central India and the Deccan, on examination at the Imperial Institute, were found to contain from 15.2 to 19.6 per cent. of tannin, while commercial samples contained 15.5 to 18.7 per cent.<sup>3</sup>

Professor Procter found this bark to yield a very unsatisfactory leather.<sup>4</sup>

*Cassia fistula*, a tree which grows freely in India, Ceylon, and Burma, yields sumari bark which is also used in India for tanning.

10. *Callitris Bark*.—The name *Callitris* has been given to a genus of coniferous plants, related to the pines, which are plentifully distributed in various parts of Australia and Tasmania. There are many species of these plants and all contain tannin

<sup>1</sup> Agric. Ledger, 1902, No. 1, 27.

<sup>2</sup> Sir George Watt, *Commercial Products of India*.

<sup>3</sup> D. B. Linaye, Bull. No. 1. Rana de Industrial and Economic Institute, Poona, India.

<sup>4</sup> Report Soc. of Arts, 1904.

in the bark, although the amount is not in every case sufficient to render them available for tanning purposes. The most widely distributed species is *Callitris glauca*, but the richest in tannin are *C. calcarata* and *C. arenosa*.

The following figures are given by H. G. Smith,<sup>1</sup> who remarks that the bark is readily stripped and would cost but little. The tannins are pale-coloured catechol tannins, and have a rapid and complete action upon the hide. These *Callitris* trees are useful in other respects since from them can be obtained valuable leaf oils (terpenes), and they also yield exudation resins closely resembling Moroccan sandarach.

TABLE XLI.—TANNIN CONTENT IN CALLITRIS BARK

Bark.	Per cent. of tannin.
<i>Callitris calcarata</i> . . . . .	19.0 to 31.2
„ <i>arenosa</i> . . . . .	25.1
„ <i>glauca</i> . . . . .	14.6
„ <i>Tasmanica</i> . . . . .	17.3
„ <i>propinqua</i> . . . . .	12.6
„ <i>gracilis</i> . . . . .	12.3
„ <i>intratropica</i> . . . . .	10.7

H. A. Coombes and A. H. Dettmann<sup>2</sup> have examined eleven samples of bark from *C. calcarata*, and six samples from *C. glauca*, which show the variation in the percentage of tannin as follows :—

TABLE XLII.—ANALYSES OF CALLITRIS BARK

	Bark from <i>Callitris calcarata</i> .			
	Tannin.	Non tannins.	Insolubles.	Water.
1	21.72	7.24	58.54	12.5
2	23.69	5.99	57.91	„
3	22.90	5.98	58.62	„
4	20.37	6.09	61.04	„
5	21.65	6.96	58.09	„
6	16.68	6.80	64.02	„
7	18.29	6.97	62.24	„
8	15.24	6.77	65.49	„
9	18.42	7.32	61.76	„
10	23.33	5.66	58.51	„
11	27.28	7.18	53.04	„
Average	20.87	6.63	60.00	„

<sup>1</sup> *Jour. Soc. Chem. Indt.*, 1911, p. 1353.<sup>2</sup> *Ibid.*, 1914, p. 232.

TABLE XLIII.—ANALYSES OF CALLITRIS BARK

	Bark of Callitris Glauca.			
	Tannin.	Non-tannins.	Insoluble.	Water.
1	15.30	5.76	66.44	12.5
2	11.03	6.30	70.17	"
3	14.63	7.02	65.85	"
4	9.02	4.90	73.58	"
5	10.99	6.55	69.96	"
6	13.00	5.03	69.47	"
Average	12.33	5.93	69.24	"

The preparation of tanning extracts from these barks appears to be worthy of attention. They impart a deep red colour to the leather, but in conjunction with other extracts they have given very good results, the leather being both solid and satisfactory with regard to weight.

11. *Hemlock Bark*.—This bark, the product of the hemlock spruce (*Abies Canadensis*, *Tsuga Canadensis*) which grows in the United States and Canada, is used in very large quantities for tanning purposes. The bark contains about 14 per cent. of tannin and an extract is made from it by the following process: The bark is first cut up into small pieces which are steeped in water at a temperature of 93° C. for about fifteen minutes. They are then fed through a hopper into a three-tier roller mill, the rollers of which are made of bronze to prevent discoloration. In this mill it is submitted to a combined pressing and disintegrating action so that the cells of the bark become ruptured and the tannin is set free. From the roller mill the material passes to an extraction plant consisting of vats in which it is treated with hot water to dissolve the tannin. After extraction the residue is raised by an elevator and delivered into a second roller mill in which the adhering solution is pressed out, the material issuing being in the form of rough sheets practically free from tannin.<sup>1</sup>

12. *Elm Bark*.—Elm bark is fairly rich in tannin, and in Chili it is one of the chief tanning agents employed. In Valdivia there are several factories which have been in operation a number of years for the manufacture of elm bark extract, which previous to the war was exported principally to Germany and France. The bark of the larch (*Larix Europæa*) also contains much tannin.

13. *Eucalyptus Barks*.—In Australia there are several species

<sup>1</sup> Spon's *Encyclopædia of Manufactures, Etc.*, 1882, p. 1985.

of Eucalyptus, the bark of which contain sufficient tannin to bring them within the category of tanning materials. The best known of these is the maletto (*Eucalyptus occidentalis*) of Western Australia, the bark of which has been cut for this purpose to such an extent during the last few years that the supply has almost entirely failed. The red gum of Western Australia (*E. calophylla*) yields a gum kino containing a considerable amount of tannin. "Tallow" wood (*E. microcorys*) bark contains 17.66 per cent. of tannin, "white or scrub gum" (*E. haestana*) bark 11.97 per cent., the inner bark of *E. Cloeziana* upwards of 20 per cent., and the entire bark of the same 11.95 per cent.<sup>1</sup> The last three being from Queensland.

14. *Tara*.—*Tara* is a tanning material which comes from Chili and Peru, in the form of pods, resembling divi-divi but paler. In Peru it is used for tanning seal skins, yielding a colour like that obtained from evergreen oak alone. It contains 30 to 35 per cent. of tanning material and a large proportion of gummy substances, which render it difficult to dispose of to extract makers, unless it be solely in admixture. It is sold in French European ports at 30 francs the 100 kilogrammes (12s. the cwt., 1908).

*Method of Using Tara*.—Take 100 butchery hides, weighing on the average 30 kilogrammes (66 lb.), or in bulk say a total of 3 metric tons, or the equivalent of this weight in cut hides, sheep skins or goat skins or any other kind of skins. To tan this quantity 600 to 700 kilogrammes (1320 to 1540 lb.) of tara will be required. Tanning is complete within four days of laying in the pit. All skins to be tanned with tara ought to be first passed through the preliminary baths, for preparing the skins, bringing them into the desired condition for being laid in the pit. The first day the skins are placed in a pit large enough to allow one or two men to manipulate them with ease. The skins are laid in the pit, folded in two, in the direction of their length, with the flesh side outwards. The tara is sprinkled on that side, placing the skins as they are usually superimposed. It is essential that, on the first day, only 100 kilogrammes (2 cwt.) of tara be used (for it contains gummy substances which harden the leather if used at first in too large amount). When the skins have been laid in the pit, they are first drenched with water previously saturated with 100 kilogrammes (2 cwt.) of tara and in sufficient amount to entirely cover the skins. The second day the skins are moved about by the workmen. This done, they are removed from the pit, taking care to shake them well, so as to cause any adherent tara to drop off, and the portion which does so is collected and run into a vat filled with

<sup>1</sup> J. C. Brunnick and A. T. Jeffries, *Queensl. Agric. Jour.*, 1916, p. 104.



water in which 50 kilogrammes (1 cwt.) of tara have been laid the previous day, so as to be well saturated therewith. Then the pit, being emptied and well cleaned, the skins are laid into it again as on the first day, spreading a layer of tara between each skin, always on the flesh side, but taking care not to place the second layer on the part which has received the first. Then the skins are drenched with water from the vat above mentioned. For the second layer, 150 kilogrammes (3 cwt.) of tara are used. The operations of the first day are repeated. On the fourth day the skins are taken out of the pit, and after being drained are placed in a bath of fresh water previously saturated with 12 kilogrammes (26·4 lb.) of alum and 6 kilogrammes (13·2 lb.) of salt, for 100 skins. The quantity of water used should be just sufficient to cover the skins; they are then worked about and withdrawn from the vat, either to be dried or curried.

15. *Mangrove*.—This tanning agent is so designated in English and in German (in French it is *palétuvier*). It is also termed "mangle," a derivation showing its origin from the *Rhizophora mangle* growing in the Gaboon, Senegal, South America, India, Madagascar. It is being marketed in increasing quantities, is a reddish, more or less pale bark, hard, and in section showing black or white spots. According to quality and origin, it contains 20 to 30 per cent. of tannin. Several foreign manufacturers have already used it in admixture in the making of quebracho extract, in which it retains its red colour and increases the tannin content of the quebracho. From experiments made by the authors to determine the value of this bark, they obtained a yield which varied between 80 and 90 per cent. of the bark treated, showing that it is a product of interest to extract manufacturers. As to its value for tanning, it is but moderate; since when used alone, it yields a soft tanned leather, but it can be used in a mixture of the following composition, which has been already utilised: 40 parts pine bark, 20 parts oak bark, 30 parts mangrove, 10 parts mimosa. Good results are also obtained by mixing mangrove extract, which can now be obtained of good quality with myrobalam, mimosa, oak, chestnut, according to the quality and nature of the skins to be tanned.

In addition to *Rhizophora mangle* there are several other trees known as mangroves, these being *R. mucronata*, *Ceriops candolleana*, *C. Roxburghiana*, and other species closely allied to these. Samples of the bark from *Rhizophora mucronata* examined at the Imperial Institute were found to vary in their content of tannin very considerably, from as low as 4 per cent. to 27 per cent., while three samples of the bark of *Ceriops candolleana* contained 17·77, 21·54, and 13·23 per cent. of tannin

respectively.<sup>1</sup> Hooper found 30.20 and 18.30 per cent. in two specimens of the latter and Professor Trimble 23.07 per cent. all on the dry bark. Mangrove cutch or solid mangrove extract is now made in India, a specimen of this product containing 76 per cent. of tannin.<sup>1</sup> This material has to a considerable extent displaced the inferior sorts of Burma cutch in the market although it differs from the latter in containing no catechin.

There is a manufactory of mangrove extract—the Mempatad Mangrove Extract Factories—in British North Borneo.

The following are analyses of mangrove barks by F. Austyn Blockey:—<sup>2</sup>

TABLE XLIV.—ANALYSES OF MANGROVE

	Tannin.	Non-tannins.	Insoluble.	Water.
<i>Rhizophora mucronata</i>	4.5	6.6	79.3	9.6
"      "	6.1	2.2	80.8	10.9
<i>Ceriops candolleana</i>	18.0	4.6	66.7	10.7

The mangrove of Venezuela (*Rhizophora mangle*) is said to contain 24 to 30 per cent. of tannin.<sup>3</sup>

16. *Catechu* or *Cutch*.—The true catechu—*gambier catechu*—is the product of *Uncaria gambier*, a small bushy tree which grows extensively wild and is also cultivated in Malacca, Singapore, and Penang. The catechu is obtained by boiling the leaves and twigs of the plant with water until the liquid attains a syrupy consistency, any insoluble particles being removed by means of a strainer. On cooling the solution solidifies, and it is then cut into small cubes which are dried on bamboo trays. Catechin contains a characteristic crystalline product known as catechu,  $C_{15}H_{14}O_6$ ,  $4H_2O$  and also catechutannic acid.<sup>4</sup> Bengal or *Acacia* catechu, and also Burma or Pegu catechu (brown catechin or cutch) are prepared from the heartwood of *Acacia catechu* which is a common tree in India and Burma, growing to a height of 30 or 40 feet. The heartwood is sawn into small pieces which are extracted with hot water. The liquor is evaporated in a very primitive manner in shallow clay pans over a fireplace excavated in the ground. After concentrating considerably the extract is decanted into larger pans and is allowed to dry spontaneously in the open air. It is stated that 1 ton of heartwood yields 250 to 300 lb. of cutch. It contains both catechin and a tannin. A third kind of catechu known as Bombay or *Areca* catechu is prepared in a somewhat similar manner from the fruit of *Areca catechu* or betel nut palm. For mangrove cutch see above.

<sup>1</sup> *Imp. Inst. Tech. Rep.*, 1903, p. 186.

<sup>2</sup> *Jour. Soc. Chem. Ind.*, 1902, p. 159.

<sup>3</sup> *Spon's Dictionary of Manufactures, Etc.*

<sup>4</sup> Perkin and Everest.

Burma produces by far the largest amount of cutch, the total annual production being estimated at from 130,000 to 150,000 cwt. In Southern India about 1000 cwt., Bombay about 500 cwt. and Bengal with the United Provinces about 20,000 cwt. make up the total.

The total exports of cutch from India and Burma were :—<sup>1</sup>

TABLE XLV.—EXPORTS OF CUTCH FROM INDIA AND BURMA

	Cwt.	Value. Rupees.
1895-6	183,729	36,96,106
1896-7	122,082	—
1897-8	97,187	—
1898-9	61,669	—
1899-00	127,815	24,70,422
1900-1	101,995	—
1901-2	66,162	—
1902-3	70,305	13,42,583
1903-4	112,936	19,71,896
1904-5	62,562	9,71,041
1905-6	97,269	15,92,561

TABLE XLVI.—CUTCH EXPORTED FROM BURMA DURING THE YEARS 1894-5 to 1906-7 <sup>2</sup>

Year.	Foreign.		Per ton.	Coasting.		Per ton.
	Quantity. Tons.	Value. Rupees.		Quantity. Tons.	Value. Rupees.	
1894-95	5524	22,34,516	404	3989	14,95,102	374
1895-96	7827	33,52,484	428	3333	13,06,637	392
1896-97	5853	22,90,365	391	1620	6,32,916	390
1897-98	4821	18,58,752	385	614	2,30,291	375
1898-99	3075	12,77,985	415	655	3,06,521	467
1899-00	6302	24,34,101	386	1159	5,76,171	497
1900-01	4949	18,42,063	372	1102	5,30,730	481
1901-02	3273	11,94,898	365	770	3,21,237	417
1902-03	3460	13,18,921	381	953	4,20,208	440
1903-04	5492	19,11,943	348	1322	5,36,387	405
1904-05	3018	9,31,596	308	779	3,12,749	401
1905-06	2723	8,48,887	311	755	3,59,069	475
1906-07	4772	15,53,470	325	868	3,61,905	417

According to the *Chamber of Commerce Journal*, March, 1917, large quantities of gambier in bales are imported into the Straits Settlements from the Malay States, British North Borneo, and Netherlands Indies, while there is a considerable export of the material to the United Kingdom, United States,

<sup>1</sup> Sir George Watt, *The Commercial Products of India*.

<sup>2</sup> R. S. Troup, *Indian Forest Records*, 1908, 1 (III).

and France. Cube gambier is also exported, principally to British India, where it is chewed like betel nut, and to Europe, America, Australia, and South Africa, for tanning purposes. Cutch is also imported into the Straits Settlements from Brunei and Sarawak and re-exported, principally to Germany before the war, but now to Great Britain. The figures for imports and exports to and from Straits Settlements are given below:—

TABLE XLVII.—IMPORTS AND EXPORTS OF GAMBIER FROM STRAITS SETTLEMENTS

	1913.	1914.	1915.	1916. (9 Months).
<i>Imports—</i>	£	£	£	£
Gambier (in bales)	208,060	170,234	293,317	251,874
<i>Exports—</i>				
Gambier (in bales)	214,535	198,404	300,261	267,187
Cube Gambier .	165,031	150,723	153,431	153,368
Cutch . . .	40,638	37,918	46,935	24,370

*R. Catechu. Special Extract for Dyeing and Tanning.*—W. Eitner remarks: "I have received a product which perfectly answers my requirements. It not only replaces japonica and other catechus, but it is also a really ideal tanning material. The manufacturers, Paul Gulden & Co., call their new product R. Catechu."

*R. Catechu. Special Extracts.*—R. Catechu is a product which can entirely replace, not only the various cutches in tanning and dyeing, but also gambier and japonica, because it possesses the properties of these different materials whilst greatly surpassing them in strength. Besides it yields better and brighter liquors, and is, moreover, much cheaper. R. Catechu does not fluctuate greatly in price like gambier and other tannins. As R. Catechu can be used in equal proportion with other tannins, it cannot only be used for all the purposes of tanning, but it may be employed preferably instead of gambier, etc., because it renders the finishing of certain leathers easier in modern methods of tanning. The proportions of R. Catechu required for tanning purposes are now given. Its use has proved to be very advantageous, especially in the preparation of new varieties of leather.

*Dyed Calf (American Method).*—The skins in bands pass through a series of vats, which are made like that with japonica and which consist, according to the weight of the skin, of six to eight liquors; the last liquor is for heavy skins, for which eight liquors of 24° Barkometer are necessary; for light skins six liquors of 24° Barkometer suffice. The striking colour is itself applied at 7° to 8°. After this tanning the leather is finished as usual. For bright colours the skin is repassed.

*Dyed Calf (Mixed Method).*—R. Catechu is of greater advantage in mixed than in ordinary tanning, and in this respect surpasses all other tanning substances. The skins in prepared bands are treated for an hour in a solution of 5 per cent. on the naked weight of salt and 2 per cent. of alum, both dissolved in fifty times their weight of water, they are then beaten for twelve hours on a block and left to stand. Tanning is done as above in six strengths, the first of which need only be of 16° Barkometer. The skin remains two days in each liquor, a solution of R. Catechu being added each day to bring the strength up to normal. To increase the strength of the tanning liquor R. Catechu dissolved in twice its weight of water is used. The complementary finishing is done as usual.

*Final Treatment of Chrome Calf with R. Catechu.*—Chrometanned leathers which have been steeped once are treated, after neutralisation and folding, with a liquor composed as follows: For 100 kilogrammes (220 lb.) of folded weight, 3 kilogrammes (6.6 lb.) of soft soap dissolved in 50 litres (11 gallons) of water, to which 600 grammes (1.32 lb.) of potash are added, then 3 kilogrammes (6.6 lb.) liquid R. Catechu, or a solution of 1.8 kilogrammes (4 lb.) of solid R. Catechu, finally 3 kilogrammes of bone-fat and  $\frac{1}{2}$  kilogramme ( $1\frac{1}{4}$  lb.) of vaseline. The skins are treated with this liquor for forty minutes to one hour in the fulling mill, they are then beaten on the block and left at rest for six hours so that they may become pliant. The skins are then stretched and dried or their working is continued. The dried leather ready for the tannery may be afterwards finished like black leather for dyeing. The latter receives in the cask, before dyeing, the final treatment with R. Catechu; in that case, for 100 lb. of folded weight 3 lb. of liquid R. Catechu are used.

*Mixed Chrome Tanning (Dongola Chrome).*—The skins in bands prepared for chrome tanning, are tanned in a simple chrome bath, i.e. with one dip. The tanning is started with a previously used chrome liquor of 12° B., adding according to the thickness of the skin gradually, in six to ten hours, 25 per cent. of the weight of the naked extract of liquid chrome (Cromal). After tanning allow to stand twelve hours on the block, then neutralise with 2 per cent. of sodium sulphide, wash, stretch, and fold. Then follows the second tanning with R. Catechu as a colour basis. The finishing colour 5°, other colours 6° Barkometer, which are kept at 6° by adding the necessary amount to strengthen the liquor. The tanning process lasts, according to the thickness of the skins, from four to twelve days. Leathers treated in this way may be prepared like "leather by measure" for current articles, that is like leathers ready for bark tanning: if leather by weight be desired they are prepared like the latter. In dyeing the glaze of the varnish, for the pre-

paration of nappa leathers, japonica or gambier was formerly used. R. Catechu produces a surprising effect, because it does not tarnish the colour, whilst it yields a pliant and elastic and at the same time a strong leather. Glacé skins are re-washed in two waters and then receive the dye bath prepared with R. Catechu and a vegetable colour; they are then steeped and afterwards passed on to be treated with the egg-yolk mixture and the final dyeing on the table. For an average skin 30 grammes (rather over an ounce) of R. Catechu are used. In dyeing with aniline dyes the leather is treated after washing only with R. Catechu. Then it is dyed with an aniline dye in the fulling mill, the colour is afterwards fixed, the leather rinsed, and finally treated with egg-yolk mixture.

*R. Catechu. A New Tanning Agent for Mixed Tanning.*—In mixed tanning two methods are used for preparing the leather, *i.e.* mineral and vegetable tanning, which are distinguished by their properties in the different processes for preparing mixed leather. As an example of mixed leather prepared by a modification of the old process, we may quote that done on the same principle as the Danish method for gloves and bandages prepared with alum and the vegetable tanning which follows afterwards, distinguished from alum leather by its softness and its strength. Eitner found in the padding of a piece of armour a mixed leather of this nature, dating, according to the archives, from the time of Marguerite Maultasch, from which it may be deduced that mixed tanning was known long ago, and that it was appreciated at that epoch. The old process of mixed tanning can now no longer be taken as the starting-point of that of to-day, as mentioned above, because it depends upon chrome tanning. As already pointed out by Eitner in his work on chrome tanning, the imperfections of this latter method of tanning have been attributed to the fact, that with this process leather cannot be obtained with its full yield and that its preparation causes difficulties; finally, a badly tanned product is the result of the action of the chrome compounds on the vegetable tan. Vegetable tanning is carried out to-day on almost all skins already treated by chrome, and on a larger scale on the leathers sold as mixed leather. Thus, with mixed leathers treated with alum, it is easy to distinguish those which have been more or less treated with vegetable tan. This replacement of mineral tanning by vegetable tanning is not easily accomplished, and drawbacks are easily encountered in experiments of this nature. One reason for this is that when vegetable tanning immediately follows the biting chrome tanning, a leather with a broken rough grain results; another reason is attributable to the fact that the right materials are not used for the purpose, which should be tanning substances yielding a soft tannin, *i.e.*

those which easily bring up the colour, but which do not tan with great rapidity. As light tanning materials capable of being used for mixed tanning, japonica, cutch, gambier, sumacs, soluble quebracho extract, and galls may be quoted. Of these substances japonica and gambier are the most often used in practice, sumacs very little, whilst galls have not yet found any safe use. Of all these materials it is R. Catechu or R. Gambier which has proved most suitable for replacing mineral tan, whilst gambier, sumac, and galls and soluble quebracho extracts are best applied in a complementary manner or as adjuncts to the catechu tanning. The easy assimilation of the tanning matters of R. Catechu has brought about the result that, after having been introduced into mixed tanning and Dongola tanning, and since their increasing use in American practice for dyed leather and black leather, prices have risen very materially, thus increasing the cost of tanning. Hence the need to seek an equivalent not only in the tannery but in dyeing, where catechu preparations have now assumed greater importance and a more extensive use even than in tanneries. Eitner is unaware whether these preparations advantageously take the place of catechu in dyeing, but in tanneries, as far as the substitutes tested by Eitner are concerned, catechu substitutes have not taken their place. In recent experiments on mixed tanning for coloured leather and for boot-making, Eitner observed that during the transition from the mineral tanning to the vegetable tanning certain kinds of cutch were more suitable than others; these are also the best for use in dyeing. These sorts are, for instance, Pegu, Coromandel, etc. They have lately been put on the market under different names and sold to consumers as catechu substitutes.

The finer qualities of catechu which are employed in mixed tanning are much less used than the inferior quality, which likewise in dyeing is only slightly valued because it has not got the same tannin content as terra japonica. Eitner found that the so-called cachou, prepared by the action of bichromate on terra japonica, scarcely tans at all in actual practice when used alone, but can be used quite well in mixed tanning. In Eitner's experiments on mixed tanning with catechu, his attention was drawn to a substance, mentioned by others as an intermediate between a tanning and a colouring principle, and which thus promised to occupy a similar position to the different kinds of catechu and prepared catechu in dyeing, for which it appeared to Eitner to act efficiently as a substitute. As a raw material for this substitute, Eitner thought of Rhizophora barks, of which mangle bark is a species, and which are to-day offered on the market under the name of tanners' mangrove. As a tanning principle, mangle or mangrove bark has not maintained its

initial price, although it has been known and "boomed" for some time. When Eitner, in 1877, gave the results of his experience of mangle, he was of opinion that in spite of its defects it would serve a useful purpose in tanning. More than thirty years have elapsed since its first use in tanning, but Eitner some time ago reported unfavourably on this bark because it had produced hollow leather. He regarded it, however, more as a dye than a tanning agent, because even in admixture with other barks it did not give good results, although the cost of the leather produced was certainly low. But in spite of its poverty in tanning substances the bark of *Rhizophora* was later found to be of great value in mixed tanning. Moreover, just as catechu is not a natural product, but a manufactured article, and only in that condition can accomplish its object, so *Rhizophora* barks are not fit to fulfil directly their part in mixed tanning without having undergone suitable preparation. Amongst the different catechu substitutes, some are to be found made from mangrove bark, in which efforts have been made to remedy the insufficiency of tanning matter by adding strengthening substances, but as Eitner found these useless in mixed tanning for the preparation of an approved product; the efforts to increase the tannin content should be discontinued and only the colouring principles contained in *Rhizophora* bark taken into consideration so as to distinguish it from real tannin extracts. Eitner received from Paul Gulden & Co., manufacturers of dye wood and tannin extracts, a product which appeared to him to have been prepared from *Rhizophora* bark, which answered his requirements, and fulfilled all the conditions of mixed tanning, not only as a substitute for japonica or other tannin extracts derived from catechu, but also as an ideal tannin. P. Gulden & Co. call this product R. Catechu, and it is put on the market in both a liquid and a solid condition. Liquid R. Catechu yielded on testing 37 per cent. of assimilable matter. This percentage agrees with that of japonica, which is regarded as a tanning agent. Eitner avoids referring to the active principle of R. Catechu, which differs from the active principle of other tanning agents. Solid R. Catechu contains about 65 per cent. of active substances, a percentage exceeding that of the better qualities of catechu. In a comparative test to determine the effects of the active substance of Pegu Catechu and R. Catechu, Eitner found them equal in the two samples: 100 parts of leather tanned by the mineral process absorbed 7.32 of Pegu Catechu, and 8.02 of R. Catechu, which gave a small difference in the weight of the skin in favour of R. Catechu. In this case the extracts were used, in proportion to their strength, in active ingredients, *i.e.* the Pegu Catechu with 50 per cent. of active substances as 100, and the R. Catechu with



65 as 80.3, *i.e.* 100 parts of Pegu Catechu are equivalent in strength to 80.3 parts of R. Catechu. Chemists may here protest that Eitner merely took Pegu Catechu and R. Catechu without proving that they resemble or are equal in chemical composition, which *a priori* is not very likely, and since, like Eitner, chemists, moreover, do not know the exact chemical nature of tanning substances, this question need not at the moment be discussed. The above practical results alone require our attention, because they are of exclusive importance in industry, these two products being about equal. With regard to the use of R. Catechu for tanning purposes, Eitner assumed that the colouring principles of the *Rhizophora*, similarly to other vegetable colouring principles, have an affinity for the tanned fibres or fabrics mordanted with metallic salts, which action does not occur at all or but little with the non-tanning substances. These colouring principles of the *Rhizophora* are therefore carried or "struck" on to the fibres of the skin, and may exercise on them an effect favourable for mixed tanning.

*Method of Using R. Catechu.*—Eitner believes that R. Catechu will prove more interesting, if mention be made of the results obtained in ordinary, *i.e.* in simple tanning. He made this test to find the independent action of the substance on the skin, both on sole leather and leather for belts. For the tests on sole leather, buff arseniated leather was used, because it appeared the most appropriate for tanning with a light tanning agent (the greater amount of buff leather is tanned with japonica, and it is perhaps so done now in Britain, if the price of japonica be not too high), since for buff leather for soles the red colour which R. Catechu gives is not only fashionable, but highly esteemed in Eitner's country. The tanning was carried out according to the British process, making the preparatory tanning of the skins, as they come out of the working in the river, *i.e.* by placing them in steep, giving for the first liquor of 8° to 16° Barkometer, and for the second 16° to 32°. After this preparatory tanning, which was accomplished rapidly and perfectly, Eitner noticed that the leather had a very fine and delicate grain esteemed in the tanning of buff-hides—an astonishing result, the more so as not having spent liquor he was obliged to use fresh juice. Instead of the three usual dips, three stronger dyes were given, because it was not desired to use any other tanning agent as a fundamental bath. The first dye was supported and strengthened for three weeks with R. Catechu, always of a strength of 35° Barkometer, the second, for three weeks, with R. Catechu of 40°, the third with R. Catechu of 45°. After ten days, the skins absorbed no more tanning matter, they were therefore taken out and finished in the usual manner. The finished leather showed on the section to be

equally tanned, was firm and soft, with the fashionable red colour, and was very thin, although not brittle. But its yield in weight was too small, being no more than 111 per cent., whilst with another tanning material it was 145 to 150 per cent. It would be impracticable to tan with such a result at the present time.

Eitner made a second experiment, but one of mixed tanning, with R. Catechu liquors, and afterwards with tannic agents like pine, quebracho, gall-nuts, myrobalam; the yield being 141.1 per cent. Carrying out the tanning in the fulling mill with quebracho and oak-wood extract, the yield was 139.5. The above results do not bring out the advantages of R. Catechu in the manufacture of sole leather; moreover, to-day, in this manufacture, no other kinds of catechu are used. The tanning of calf skins for leather, dyed according to the American method, has proved very satisfactory. The preliminary and the final tanning are done in the same way, with known catechu liquors, only it is necessary to work with stronger liquors to produce the same effect. For japonica, liquors of 18° Barkometer strength suffice; for catechu, to secure the same effect, liquors of 24° are required, without any superior tanning being obtained. For tanning with R. Catechu, a stronger depilatory is needed. The leather obtained, judging from these experiments, had all the properties of leather tanned with japonica, the reddish colour of which does not disturb the dyeing; and, as on selling, the weight is not taken into consideration, R. Catechu may be employed in place of japonica or gambier, which costs more. R. Catechu is advantageously used in the case of white leathers with mixed treatment. To judge this better, samples were prepared with japonica and nut-galls. For these tests, calf skins of an average weight of 3.6 kilogrammes (8 lb.) per piece were taken. After washing for two days, they were unhaired for five days in a lime depilatory, then five other days in a new, fresh, and suitable lime, after which they were well cleaned and placed in bran. After removing the skins from the bran, they were weighed and laid in the preliminary preparation vats. The latter being composed of a solution of 5 per cent. of common salt and 1 per cent. of alun. These substances were left to dissolve in fifty times their weight of water, and it was with this solution warm that the skins were treated in the vat for an hour. The amount of alun used being very small, only a very thin alun tanning is obtained, which may be regarded simply as a steep, for raising the colour. But this previous steep sufficed already to bring out, in quite another way, the effect of R. Catechu. Afterwards the skins were beaten on a block, and left to stand all night, an operation similar to the aeration of tanned goods in getting up the colour. Then commenced the

vegetable tanning of the skins, which were all treated in the same manner. Tanning was done with *R. Catechu*, *japonica*, and a fresh extract of nut-galls, or *valonia*, prepared cold. The first colour was given in three experiments of 6° Barkometer, and every second day the strength of the steep was increased 1°. So that the strength of the liquors on the third day was 7° and the fifth day 8°. The strength of the last liquors was, in the three parallel experiments, 15°, and the whole of the tanning was completed in twenty days. In actual practice the time may be reduced to twelve to fourteen days, especially if, towards the end, the strength of the liquor is increased daily.

After this tanning the three sorts were worked together as follows: After rinsing, the skins were washed with a 1 per cent. solution of monopol soap; they were then treated with a mixture of monopol soap and sod oil, and finally dried. The further currying was done on dyed and satin leather, tanning the first after folding with 200 grammes of sumac, and dyeing them. Once finished, the skins with *R. Catechu* were in each unhairing the best; one could, moreover, observe it after tanning, and possessing the means of comparison, Eitner was entirely convinced that *R. Catechu* should be preferred for tanning dyed leather and leather for boots. Later on, he succeeded in imparting special properties to the leather, by modifications in the preparation of the salt and the preliminary steep. In the mixed tanning described, the alum tanning was less important than the succeeding vegetable tanning. Another test had quite a contrary object, the mineral tanning with alum liquor predominated, and the vegetable tanning only served to modify the properties of the leather. As the curriers make such leathers as "Dogskin" and "Nappa," the nappa was the object of this test. The experiments with *R. Catechu* on chrome-tanned leather, after final treatment, will now be described. As already mentioned, all chrome-tanned leathers, the grain of which has been specially prepared, such as boxcalf and other sorts, receive a further vegetable treatment, the object of which is to re-tan the grain alone with vegetable matter, that being more readily applicable to a "Shagreen" finish. This retouching is somewhat difficult, for chrome tanning yields a brittle grain of poor durability, whilst vegetable tanning causes the property of the chrome-tanned leather to disappear more or less. In experiments made with calf, horse, and sheep skins, the one-steep or dip method was adopted, as being more favourable and less dangerous than the two-dip method. The following is approximately the method adopted. The skins were laid in a lime depilatory, twice renewed, unhaired, washed, and scraped, the grain formed, and then steeped in Picol's liquor; they were then chrome tanned with Cromul A for horse-hides and calf-

skins, with Cromul B for sheep and goat skins (250 grammes of cromul being added per kilogramme of skin to the old liquor). After tanning in the pit, the skins were allowed to stand for twenty-four hours; they were then drawn through Vaughan's machine, and finally folded. Skins intended to be dyed black were steeped in logwood liquor in the vat; they were then tanned with vegetable tannin, and oiled (*tannage de graisse*). As liquor the following are the proportions per cent. by weight of the fold: 3 kilogrammes (6.6 lb.) of Licker's fat soap dissolved in 50 litres (11 gallons) of water for boxcalf and Hochlanzleder; 600 grammes (1½ lb.) of potash were added, then 3 kilogrammes (6.6 lb.) of liquid R. Catechu, or 1.8 kilogrammes (4 lb.) of solid, dissolving the latter in hot liquor; for finishing, 3 kilogrammes (6.6 lb.) of bone fat and 500 grammes (1.1 lb.) of vaseline were added (Dermolin). The skins were treated with this mixture in the vat from forty minutes to an hour, according to the kind of skin: sheep and goat skins were less than forty minutes, heavy calf and horse-hides one hour. Horse-hides were treated with 4 per cent. of soap instead of 3 per cent., the other ingredients being increased in proportion. After this treatment the leathers were left for five to six hours and dried. The dried leather was repassed, oiled with bone fat mixed with 5 per cent. of glycerine, then redried. After drying, the leather was blackened with Carvoline B on the grain, and afterwards finished as usual. Skins to be coloured were treated as aforesaid. After folding, they were uniformly dried. By working thus chrome-tanned leather is obtained as dry as vegetable-tanned leather; the same is the case in the dyeing, which cannot be done otherwise. The dried leathers were fulled for dyeing in hot water; the skins intended for bright colours may be prepared with 60 to 80 grammes of sumac. Washed once, they are dyed. If the leather is not to be dyed a bright colour R. Catechu may be advantageously used in place of sumac since it greatly helps in the dyeing; good-covering and well-fed shades being obtained, impossible to realise with simple chrome tanning. For the final treatment with R. Catechu, 3 per cent. on the folded weight of the leather was dissolved in 100 times its volume of water. The leather was fulled in this very weak liquor for about an hour and then placed in the dye bath. For dyeing, all the colours used for sumac-tanned leather, acid as well as basic, may be used, and there is no need to dry the dyed leather after treating with the liquor.

Having thus obtained good results with R. Catechu, the use of this product in mixed tanning has been passed in review. This tanning process, by which Dongola leather is made, is highly spoken of at the present time, and it is used for calf and sheep skins, but chiefly for kips, horse leather for boots, ox-

hides, and spaltes. Very soon a great revolution will take place in the manufacture of kips, because, in the same way as in the sale of uppers, the manufacture of leather increases by mixed tanning. There is a considerable importation of American uppers made by this method of mixed tanning; it is therefore time that more attention was given to this method of tanning, which has the advantage of being cheap. The following are more exact experiments in this line: as raw material a low quality of C.C. kips, weighing 2.5 kilogrammes, and also horse necks were employed. The treatment of the kips was as follows. For two days they are stretched in a vat already used, but rather strong, then revatted with 20 per cent. of sodium sulphide on the weight of the raw leather. After vatting they were left eight days in a lime depilatory, then four days in a fresh lime depilatory (proportion 5 per cent. of the raw leather). After washing and scraping, they were placed for two hours during the night in a bran steep (15 litres of bran per 100 kilogrammes of raw goods), then inserted in a picol steep (1 per cent. of picol on the naked weight) for one hour, then chrome tanned. Commencing with a chrome liquor already used, of 12°; adding gradually during six hours 25 per cent. of Cromul A; the skins were laid on the block and left for twelve hours. Neutralised with 2 per cent. of the naked weight of sodium sulphide (1 of sodium sulphide in 100 of water) for two hours, washed, stretched, folded, and finally dyed in R. Catechu. This final tanning is preferably done with bright colours, or failing these, with colours which may be enhanced. The first dye was given with 5° R. Catechu, which after two hours fell to 2°; it was then brought to 6°; after twenty-four hours it fell to 3°; it was again brought to 6°; after four days the tanning was finished; 30 per cent. on the naked weight of R. Catechu being used. In practice the consumption fell to 25 per cent. In the final tanning the vegetable matter very soon traverses the skins. It always penetrates, in the same way, so that in each phase of the tanning process a method of comparison is at hand by which the strength of the vegetable tanning may be increased or diminished according to the properties to be imparted to the leather. A very interesting point in this tanning is that it is done with very weak liquors, but nevertheless the skins very quickly absorb the active substance; moreover, there is no need to increase the strength in the final stages, a fact which does not coincide with the rules of vegetable tanning. This peculiarity of R. Catechu renders it possible to work the skins uniformly, and they can easily be submitted to the final vegetable tanning. In regard to kips they are treated similarly, and further they are washed and stretched. The increase of weight of the chromed leather was almost 4 per cent. after treatment

with R. Catechu, and it could still assimilate tanning substances. To prove this Eitner took a portion and treated it with 20 per cent. of chestnut extract and 20 per cent. of liquid quebracho. These leathers, retanned for six hours in a liquor of 20° to 25° Barkometer, prepared as usual, gave a yield of 142 per cent. after uniform oiling. They were soft, full in the section, very uniform, very soft on the flesh side, and their colour, in spite of the chrome treatment, showed no difference from bark-tanned leather. There can therefore be produced by mixed tanning with R. Catechu a heavy, full leather of good appearance and properties, which, in spite of the tanning with chrome, resembles that of bark; finally this tanning is cheap and rapid. The other kips treated only with R. Catechu were washed, beaten, and weighed. The liquor for these consisted of 3 per cent. of Licker's soap, on the already indicated weight of the leather, dissolved in 30 per cent. of water; 6 per cent. of sod oil was added afterwards to this soap solution. The skins were dipped for one hour at a temperature of 30° R. After this liquoring the skins were drained and dried. Eitner, working in different ways on leather of defective grain, produced "varnished leather," "dull sole," "boxcalf," and "round grain"; all of which were easily produced owing to the mixed process of tanning used. These results are highly important, since they enable inferior products to be used, whilst chrome tanning requires first class materials. Horse necks, ox-hides or sheep skins may be tanned very advantageously for kips by R. Catechu both as regards quality of product and yield. It is the same with varnish leathers, or for other purposes in which R. Catechu is capable of playing an important part. For all these reasons manufacturers should give their attention to this product which is known as R. Catechu in Germany, and R. Gambier in Britain.

## CHAPTER IX

### MANUFACTURE AND USE OF LOGWOOD EXTRACT

#### WOOD EXTRACT

*Logwood or Campeachy Wood.*—The wood of *Hæmatoxylon campechianum*, a tree belonging to the family Cæsalpinia of South America and East Indies. The chief varieties are: the cut logwood of Spain, Mexican logwood, St. Dominica or Hayti logwood, Honduras logwood, Martinique logwood, Guadeloupe logwood, Cape, etc., logwood. It appears in commerce as large logs or trunks (Laguna), or as branches and roots which are cut into chips with a cutting machine similar to that shown in Figs. 91 and 92. Disintegration costs one franc per 100 kilogrammes (5d. per cwt.). Hæmatoxylin ( $C_{16}H_{14}O_6 \cdot 3H_2O$ ) is the active principle contained in logwood, which, by oxidation in the air, or in presence of alkalis, is transformed into hæmatein, the real colouring principle  $C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2O$ ). Hæmatein yields coloured lakes with metallic salts, the most important of which, those of iron and chromium, are much used in dyeing black and dark colours. Alkalis change hæmatein solutions from red to reddish-violet, whilst acids bring them back to yellow again; concentrated acids turn them red. The value of logwood depends on its hæmatein content. The following table gives the figures obtained by L. Bruel with different brands:—

TABLE XLVIII.—SHOWING YIELD OF AQUEOUS EXTRACT FROM VARIETIES OF LOGWOOD WITH PERCENTAGE OF HÆMATEIN IN EXTRACT

Brand.	Aqueous Extract per cent.	Hæmatein in Aqueous Extract per cent.	Brand.	Aqueous Extract per cent.	Hæmatein in Aqueous Extract per cent.
Yucatan .	20.20	37.46	Monte Cristo	18.75	60.32
Laguna .	21.00	47.95	Fort-Liberté	20.30	54.11
Dominica .	14.02	53.47	Jamaican .	18.70	50.50

*Drenching and Preparing the Wood.*—For this operation the logwood chips should be piled in layers of 50 to 60 cm. (20 to 24 inches) thick, and so placed in a sufficiently capacious space



that they may be turned easily and frequently. Drenching is carried out, according to the nature of the wood and the use to which it is to be put, either with pure water or water to which there has been added either lime, yellow prussiate, permanganate, carbonate of soda or sodium peroxide. The wood is generally sprinkled with lime water (0.5 per cent. of lime) or with a solution of potassic chlorate and oxalic acid (0.25 per cent. of each), bichromate of potash (1 per cent.), or carbonate of soda (0.25 per cent.). The proportion employed may vary from 1 to 4 per cent. of water, and the length of the fermenting process from two to ten days. The operation should be pushed to the extreme, when the wood is intended for extraction, in small autoclaves or "pears," or even when intended to be used directly in the dye vats. This operation facilitates the development of the colouring principle by converting the hæmatoxylin into hæmatein, renders the latter more easily assimilated by the water, and enables dyers to proceed with a rapid extraction in a small quantity of water without much loss. For the same reason, the treatment of the wood under pressure, in close vessels, ought always to be preceded by rational preparation, for, in this case, it is important to work with as small a volume of water as possible, so as to obtain strong liquors, which constitute the real economical principle of the system. However, in an important factory, it would not be possible to keep wood in preparation for eight to ten days. The difficulty is obviated by the intervention of certain oxidising agents to hasten the fermentation. According to the wood, its nature, its freshness as shown by a section, the kind of extract to be made (ordinary extract or oxidised extract, Huillard & Co.'s sort), the length of the preparation, the product or products to be used, and the proportions of the latter, which are very variable, are not at all definite, and it is only the manufacturer who can judge the degree of fermentation required. In the manufacture by continuous decoction—in open vats—the fermentation should not be too prolonged, because the frequent contact of the liquor with the surrounding air gives rise to a natural oxidation, which, together with the previous oxidation, may lead to a perceptible loss of colouring matter. In such cases forty-eight hours' fermentation suffices. This last system of extraction is certainly much the simplest, most practical, and economical. The manufacture, if properly conducted, gives good yields, and extracts quite as strong, which have at least as much body as those made under pressure. On the other hand, the latter have more freshness of tone and are more easily assimilated by textile fibres; in terms of the trade they draw more quickly.

*Manufacture of Logwood Extracts.*—As just stated, in a general way, logwood is extracted in open vats, the yields



obtainable being a factor of the varieties or qualities treated, the preparation which they have undergone, and the successive washings used in maceration. In France open vats are used for maceration, but in America the material is heated with water under pressure. As in the case of oak-wood extract, logwood requires almost the same plant, except that the evaporation or concentration of the liquor is best effected in as complete contact with the surrounding air as possible, so as to facilitate the conversion of the glucosides into colouring principles. To effect this the old factories, and even some existing ones, still utilise the lens apparatus, which vaporises 0·7 kilogramme of water per kilogramme of steam consumed, whereas the ordinary triple effect evaporates 18 to 20 litres of water by the consumption of 7 kilogrammes of steam or about 1 kilogramme of coal.

*Yields.*—These, as already mentioned, are very variable for the reasons stated; nevertheless, those obtained by the authors are given here, using nitrite of soda as an oxidising agent, in the proportion of 0·5 kilogramme per 100 kilogrammes of logwood chips (say  $\frac{1}{2}$  lb. per cwt.) and in the maceration of a variety of Cape roots.

TABLE XLIX.—YIELD OF LOGWOOD BY EXTRACTION IN OPEN VATS

	A.	B.	C.	D.
10° extract per cent. of wood treated . . . .	74·0	55·0	—	67·5
30° " " " " " " " " " " " " " " " "	24·5	18·0	20·0	22·5
Dry " " of 10° " extract . . . . .	18·5	17·6	—	17·8
" " " " 30° " " " " " " " " " "	55·0	52·5	53·2	54·0
" " " " of wood treated . . . . .	13·7 $\frac{1}{2}$	9·7	10·5	12·0
Kg. wood required to produce 100 kg. 10° extract .	135	181	166	148

A, Variety not given; B, "Aquin" logwood in logs; C, "Cayes" logwood in long logs, hard to grind, rapidly exhausted; D, Cape roots.

It is certain from the above industrial yields that the addition of oxidising agents to the maceration of the different qualities of logwood if properly regulated contributes greatly to an increased yield, but may on the other hand lead to loss and has been largely discontinued, but that ought not to prevent selection in buying certain sorts in preference to others, the origin of which already indicates to a certain extent the percentage of hæmatein. On the other hand, roots should be preferred to logs, except as regards Laguna, which up to now is one of the best qualities reaching Havre; it is more costly accordingly. A variety of dry extract is found in commerce termed "resinous," which is deposited in the decantation vats, a product due to simple desiccation by the steam of the resinous matters which are deposited in the decantation vats for the 10°

or 15° extract. Weak extracts deposit in winter as much as 9½ per cent. but in summer only 5 per cent., and these resinous substances are capable of yielding 10° extract once more by re-dissolving them in hot water and filtering, so as to separate the wood dust and other solid impurities. The following is the average composition of these dry resinous extracts:—

TABLE L.—SHOWING COMPOSITION OF RESINOUS DEPOSIT FROM LOGWOOD EXTRACT

	Per cent.
Dry soluble extract . . . . .	60.0
Water . . . . .	22
Insoluble . . . . .	18
	<hr/> 100.0

*Data Relating to 10° Logwood Extract:—*

Resinous pasty extract per cent. of 10° extract . . . . .	9.5
Dry resinous extract per cent. . . . .	7.7
" " " of pasty extract . . . . .	80.0
Percentage of 10° extract from resinous pasty extract . . . . .	150.0

*Remarks.*—As mentioned above, oxidised extracts yield deep shades in dyeing, but less fast to washing, air, light, and chlorine; they have some advantages when used directly in dyeing black. Highly oxidised extracts give bad results in calico printing. In buying logwood extracts, the purchaser should be very cautious, for they are frequently adulterated. The colouring principle should always be estimated, and a dye test made with different mordants so as to determine its value.<sup>1</sup> The substances most often used to adulterate logwood extract are chestnut extract, molasses, dextrine, and salt. Sandfort logwood contains, for instance, 50 per cent. of pure extract, 25 per cent. of molasses, 10 per cent. of dextrine, 12 per cent. of chestnut extract, and 3 per cent. of salt. There is at present on the market, under the name of hæmatein or chrysohæmatein, a logwood extract of great purity. British hæmatein contains 95 per cent. of colouring principle (hæmatoxylin and hæmatin). American hæmatein contains 60 per cent., and French hæmatein 75 per cent. The chief French makers of logwood extract are Watrigant et Fils, of Marquettes-lez-Lille; Compagnie Française des Extraits Tannants et Colorantes, of Havre. The exports of logwood from Jamaica in 1916 amounted to 74,157 tons and 28,477 packages of logwood extract.

R. H. Wisdom<sup>2</sup> found that logwood, when examined by the official method of the American Leather Chemists Association, showed an apparent tannin content of 7.82 per cent. with non-tannin 5.83 per cent. Similarly a pure clarified logwood extract

<sup>1</sup> See "Use of Logwood in the Tannery," by H. Jossiar, *Bull. du Synd. Gén. de l'Industrie des Cuirs et Peaux*, June 10, 1901.

<sup>2</sup> *J. Amer. Leather Chem. Assoc.*, 1913, p. 274.

yielded 23.9 per cent. of tannin and 20.8 per cent. of non-tannin, and he suggests that logwood could be used in partial replacement of tannin extracts for the tanning of leather which is afterwards to be dyed black for instance. He also affirms that an excellent leather has been produced with logwood extract.

### WOOD EXTRACT

The liquors obtained in the preparation of wood pulp from spruce, pine, and fir wood by heating with bisulphites under pressure contain the products of the lignone constituent of the original material in a soluble form, but not profoundly modified since very little chemical action takes place in the process. We have therefore present the furfural-yielding constituents, carbohydrates of the nature of wood gum, and also the keto-R-hexene product referred to by Cross and Bevan as being a constituent of all lignocelluloses, including woody tissues.

For a long time these liquids were run into the nearest stream or river, or, in a few cases when sodium bisulphite (but more particularly caustic soda) had been used they were evaporated and calcined for the regeneration and utilisation of the sodium compound, a useful although not very remunerative proceeding. Owing, however, to the nuisance eventually arising from the pollution of such streams, but also more often to the pressure applied by sanitary authorities demanding the abatement of such nuisances, it became urgently necessary to deal with these liquids in a much more rational fashion.

The liquids are therefore now filtered, concentrated in one of the forms of vacuum driers already described, and the salts which have separated are strained out.

The product thus prepared is a thick, dark brown, very heavy fluid extract known as "wood extract" in this country, and as "Fichtenholz" in Germany. Large quantities of this material are now available at a very moderate price, and it has been recommended for a variety of purposes including tanning. It is, however, not a tanning material in the strict sense of the word as it contains practically no tannin, and when used alone fails to convert hide into leather, the product being very poor, hard, bony, and extremely light. Eitner found that the skin, after treatment with this material, contained only 0.5 per cent. more dry material than the original hide. This result has been confirmed by other observers. On the other hand, when used in conjunction with tanning extracts, it acts as a plumping and weight-adding material, this being confirmed by the fact that when tested by the official method of the I.A.L.T.C., a considerable percentage of it is absorbed by the hide powder, as shown by the following analyses by Eitner.

TABLE LI.—ANALYSES OF WOOD EXTRACT

Wood Extract.	Substances Removed by Hide Powder.	Substances not Removed by Hide Powder.	Water.	Ash.
Hungarian extract	22.8	27.5	49.6	5.32
German        "	22.6	28.2	49.0	—
Excelsior     "	25.8	28.0	46.2	7.50

Owing to this behaviour of wood extract there is considerable difficulty in detecting its presence in mixed extracts or in cases where it is used for sophistication, and it is practically impossible with the hide-powder method. This being the case, the test for wood extract devised by Professor Procter and S. Hirst<sup>1</sup> is all the more valuable. This test is a modified lignin test in which the aniline hydrochloride reaction is utilised. The test being carried out as follows: 5 c.c. of the dilute extract of about the same strength as that used for the estimation of tannin is taken, to this is added 0.5 c.c. of aniline and the whole thoroughly shaken, then 2 c.c. of concentrated solution of hydrochloric acid is run in which immediately dissolves the aniline thus removing the turbidity, so that with ordinary tannin extracts a perfectly transparent solution results. If, however, even a small quantity of wood extract is present it causes a precipitate to form which soon rises to the surface of the liquid and is readily distinguished. Heating of the liquid is not required nor is it recommended, and no account should be taken of any precipitate which may subsequently form since this might occur with other extracts.

The above authors also draw attention to the fact that wood extract has very little action upon a dilute solution of permanganate, thus an extract which shows about 25 per cent. of matters absorbed by hide powder gave only the equivalent of 4 per cent. of gallotannic acid by Löwenthal's process, so that any marked discrepancy of this kind between the gravimetric and Löwenthal's process would point to the presence of wood extract in the sample under examination. Tests for furfural and other aldehydes in wood extract gave negative results.

<sup>1</sup> *Jour. Soc. Chem. Indt.*, 1909, p. 293.

## CHAPTER X

### OFFICIAL METHOD OF TANNIN ANALYSIS OF THE INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMISTS

It has been decided by the conference, Brussels, 1908, that any method which conforms to the conditions of paragraphs 1 to 4 of the following statement may be regarded as conforming to the recommendations of the International Commission on Tannin Analysis, but that members of the International Association must work according to the detailed directions contained in paragraphs 5 to 8.

*Paragraph 1.*—The solution for analysis must contain between 3.5 and 4.5 grammes of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50° C., but if the Teas extractor be used, the first portion of the extract shall be removed from the influence of heat as soon as possible.

*Paragraph 2.*—The total solubles must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cm. thickness, and a layer of 1 cm. deep in a beaker, placed in a good light on black glass or black glazed paper, must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution, a correction must be determined and applied as described in paragraph 6. Filtration shall take place between the temperatures of 15° C. and 20° C. Evaporation to dryness shall take place between 98.5° C. and 100° C. in shallow, flat-bottomed basins, which shall afterwards be dried until constant at the same temperature, and cooled before weighing for not less than twenty minutes in air-tight desiccators over dry calcium chloride.

*Paragraph 3.*—The total solids must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution, at a temperature between 98.5° C. and 100° C. in shallow, flat-bottomed basins, which shall afterwards be dried till constant at the same temperature, and

cooled before weighing for not less than twenty minutes in an air-tight desiccator over dry calcium chloride. "Moisture" is the difference between 100 and the percentage of total solids, and "insoluble" the difference between the total solids and total solubles.

*Paragraph 4. Non-Tannins.*—The solutions must be de-tannised by shaking with chromed hide-powder till no turbidity or opalescence can be produced in a clear solution by salted gelatin. The chromed powder must be added in one quantity equal to 6.0 to 6.5 grammes of dry hide per 100 c.c. of tanning solution, and must contain not less than 0.2, and not more than 1 per cent. of chromium, reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water not more than 5 milligrammes of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder should be determined and allowed for as water of dilution.

*Paragraph 5. Preparation of Infusion.*—Such a quantity of material shall be employed, as will give a solution containing as near as possible 4 grammes of tanning matter per litre, and not less than 3.5 or more than 4.5 grammes. Liquid extracts shall be weighed in a basin or beaker, and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed, and rapidly cooled to a temperature of 17.5° C., after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials, previously ground till they will pass through a sieve of 5 wires per centimetre, are extracted in Koch's or Procter's extractor with 500 c.c. of water, at a temperature not exceeding 50° C., and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than three hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as "difficultly soluble" substances. The volume of liquid in the flask must, after cooling, be accurately made up to 1 litre.

*Paragraph 6. Filtration.*—The infusion shall be filtered,

repeatedly if necessary, till optically clear. No correction for absorption is needed for the Berkefeld candle, or for S. and S. 590 paper if a sufficient quantity (250 to 300 c.c.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate.<sup>1</sup> If other methods of filtration are employed, the average correction necessary must be determined in the following manner. About 500 c.c. of the same, or a similar, tanning solution is filtered perfectly clear, and after thorough mixing 50 c.c. is evaporated to determine "total soluble No. 1". A further portion (of the filtered solution) is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible), and 50 c.c. is evaporated to determine "total soluble No. 2". The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c.c. and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.c. of the clear filtrate, obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

(*Note*.—It is obvious that an average correction must be obtained from at least 5 determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. and S. 605, 150 c.c. being rejected, to about 5 milligrammes per 50 c.c. and where 2 grammes of kaolin are employed in addition to  $7\frac{1}{2}$  milligrammes. The kaolin must be previously washed with 75 c.c. of the same liquor, which is allowed to stand fifteen minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.)

*Paragraph 7.*—Hide-powder shall be of a woolly (fibrous)

<sup>1</sup> It was important to clearly define the conditions under which filtration should be carried out. It has, in fact, been demonstrated that all filtering substances, such as paper, kaolin, and even sand, absorb variable proportions of tannin. See Searle, *Influence of the Substances Used in the Determination of Soluble Matters*, H. a. C., 1900, pp. 731 and 747. On the other hand, certain solutions of tannin remain turbid for a long time, and it is impossible to clarify them by deposition. At the Liège Congress of 1901, Dr. Paessler stated as the results of experiments that filter paper No. 605 was not always uniform; in spite of which, the use of this paper was continued to the Leeds Congress of 1902, where the difficulty was to be settled. Dr. Paessler comparatively tested the use of Schleicher and Schull's filter papers No. 597 and 602, and found very notable differences in the results obtained, according to which number was used (*Zeit. f. Ang. Chem.*, 1900, p. 318, or *Monit. Quesn.*, 1901, p. 395).

texture, thoroughly delimed, preferably with hydrochloric acid, and shall not require more than 2.5 c.c. of N/10 NaOH or KOH to produce a permanent pink with phenolphthalein on 6½ grammes of the dry powder suspended in water. If the acidity does not fall within these limits, it must be corrected by soaking the powder before chroming for twenty minutes in 10 to 12 times its weight of water, to which the requisite calculated quantity of standard alkali or acid has been added. The hide-powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70 to 75 per cent. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 milligrammes per 100 c.c. The powder when sent out from the makers shall not contain more than 14 per cent. of moisture, and shall be sent out in air-tight tins.

The detannisation shall be carried out in the following manner:—

The moisture in the air-dried powder is determined, and the quantity equal to 6.5 grammes actual dry hide-powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and wet back with approximately ten times its weight of distilled water. 2 grammes per 100 of dry powder of crystallised chromic chloride  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is now dissolved in water and made basic with 0.6 gramme  $\text{Na}_2\text{CO}_3$  by the gradual addition of 11.25 c.c. of N/1 solution, thus making the salt correspond to the formula  $\text{Cr}_2\text{Cl}_6(\text{OH})_3$ . The solution is added to the powder, and the whole churned slowly for one hour. In laboratories when analyses are continually being made, it is more convenient to employ a 10 per cent. stock solution, made by dissolving 100 grammes of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in a little distilled water in a litre flask, and very slowly adding a solution containing 30 grammes of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution, 20 c.c. per 100 grammes or 1.3 c.c. per 6.5 grammes of dry powder should be used.

At the end of one hour the powder is pressed (squeezed in linen) to free it as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water, until on adding 50 c.c. of the filtrate, 1 drop of 10 per cent.  $\text{K}_2\text{CrO}_4$  and 4 drops of N/10  $\text{AgNO}_3$ , a brick-red colour appears. Such a filtrate cannot contain more than 0.001 gramme of NaCl in 50 c.c.<sup>1</sup>

<sup>1</sup> For the accuracy of the I.A.L.T.C. method of estimating tannin, see Professor H. R. Procter's *Collegium*, 1909, iv., 17; *Jour. Soc. Chem. Indt.*, 1909, iv., 15.



The powder is then squeezed to contain 70 to 75 per cent. water, and the whole weighed. The quantity  $Q$  containing 6.5 grammes of dry hide is thus found, weighed out, and added immediately to 100 c.c. of the unfiltered tannin infusion along with  $26.5 - Q$  of distilled water. The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute. It is then squeezed immediately through linen, stirred, and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 c.c. of the filtrate is evaporated and reckoned as 50 c.c. or the residue of 50 c.c. is multiplied by  $\frac{5}{3}$ . The non-tannin filtrate must give no turbidity with a drop of a 1 per cent. gelatin, 10 per cent. salt solution.

One gramme of kaolin free from solubles must be used either by mixing it with the hide-powder in the shaking bottle or with the liquid before filtration.

*Paragraph 8.*—The analysis of used liquors and spent tans shall be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being diluted, or concentrated by boiling in vacuo, or in a vessel so closed as to restrict access of air, until the tanning matter is if possible between 3.5 and 4.5 grammes per litre, but in no case beyond a concentration of 10 grammes per litre of total solids, and the weight of hide-powder used shall not be varied from 6.5 grammes.

The results shall be reported as shown by the direct estimation, but it is desirable that in addition efforts shall be made by determination of acids in the original solution, and in the non-tannin residues, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide-powder and hence returned as "tanning matters". In the case of tans it must be clearly stated in the report, whether the calculation is on the sample with moisture as received, or upon some arbitrarily assumed percentage of water; and in that of liquors whether the percentage given refers to weight or to grammes per 100 c.c.; and in both cases the specific gravity shall be reported.

*Paragraph 9.*—All evaporation shall be rapidly conducted in steam temperature in shallow, flat-bottomed basins of not less than 6.5 cm. diameter to apparent dryness; and shall be subsequently dried between  $98.5^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ . in a water or steam oven until of constant weight, and shall be afterwards cooled in small air-tight desiccators over dry calcium chloride for at least 20 minutes, and then weighed rapidly. Not more than two basins shall be placed in one desiccator, and the basins must not be wiped after removal from the desiccator.

All analyses sent out by members or associates of the I.A.L.T.C. should be made in exact accordance with the preceding regulations, and described as "Analysed according

to the Official Method of the I.A.L.T.C.," but if for any cause another method must be adopted, the exact method used, and the reasons for its employment shall be distinctly stated, such descriptions as "old official method" being prohibited. Any copy or copies of the report of analysis, whether furnished by the analyst, or his client and agents, shall contain the entire matter both written and printed of the original report.

All analyses reported must be the average result of duplicate determinations which must agree in the case of liquid extracts within 0.6 per cent., and of solid extracts within 1.5 per cent. or the analysis shall be repeated till such agreement is obtained, and it must be clearly stated on the report that the results are the mean of such corresponding determinations.

OFFICIAL METHODS OF THE AMERICAN LEATHER CHEMISTS  
ASSOCIATION FOR TANNIN ANALYSIS

1. *Crude Materials*

(1) *Moisture Determination*.—Upon receipt of the sample, grind promptly and dry 10 grammes in the manner and for the period specified for evaporation and drying in extract analysis.

(2) *Preparation of Sample for Extraction*.—Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(3) *Amount of Sample and Proportion of Water for Extraction*.—For fresh materials the amount of sample and proportion of water for extraction should be such as to give between 0.35 to 0.45 gramme tannin per 100 c.c. of solution. For spent materials this should be approximated as closely as practicable.

(4) *Extraction of Sample*.—Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued until a portion tested with gelatin salt solution fails to give a precipitate. At least 500 c.c. of the first portions of extractive solution should be removed, and not subjected to further heating. A thin layer of cotton must be used, in order to prevent fine material passing over.

(4a) *Sumach and Kindred Materials*.—Put the material (the amount should be such as to give between 0.35 and 0.45 gramme of tannin per 100 c.c. of solution) in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, cover it with water, and allow to soak for one hour. Then extract by collecting 2000 c.c. of the extractive solution outside through lower tube, in from six to eight hours. Let the extractive solution stand overnight,

and analyse the following day by the Official Method for Extracts.

(5) *Analysis*.—After extraction and dilution, solutions must be heated to 80° C. and analysis conducted as per Official Method for Extracts. In the case of weaker dilutions than the Official Method specifies, the amount of hide-powder must be reduced in proportion to the reduction in tannin.

Ten grammes of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted, and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received".

## II. ANALYSIS OF EXTRACTS

(6) *Amount and Dilution for Analysis*.—Fluid extracts must be allowed to come to room temperature, and weighed in stoppered weighing bottles. Such quantity shall be taken as will give from 0.35 to 0.45 gramme of tannin per 100 c.c. of solution. Dissolve in exactly 900 c.c. of distilled water at 80° C., and make up to mark after standing not more than twenty hours, nor less than twelve hours. Temperature must not go below 20° C.

(7) *Total Solids*.—Thoroughly mix solution, pipette 100 c.c. into a tared dish, evaporate and dry as directed under "Evaporation and Drying".

(8) *Soluble Solids*.—To 1 gramme of kaolin in a beaker add 75 c.c. of solution; stir and pour on a "590 S. and S." 15 cm. plaited filter-paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 c.c. of solution to 20° C., refill the filter with this solution, and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 c.c. of filtrate, as per "Evaporation and Drying".

(9) *Non-Tannins*.—A quantity of hide powder, sufficient for the number of analyses to be made, shall be prepared in the following manner: Digest with ten times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours, and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press if necessary, so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 grammes of the wet hide for moisture determination. Add to 200 c.c. of the original solution such quantity of the wet hide as

represents from 12 to 13 grammes of dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grammes kaolin to the filtrate, stir, and filter through folded filter (No. 1 F Swedish recommended) of size sufficient to hold entire filtrate returning until clear. Evaporate 100 c.c. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide-powder.

*Note.*—In order to limit the amount of dried hide-powder used, determine the moisture in the air-dried powder and calculate the quantity equal to  $12\frac{1}{2}$  grammes of actual dry hide-powder. Take any multiple of this quantity, according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 to 75 per cent. water. Weigh the whole amount and divide by the multiple of the  $12\frac{1}{2}$  grammes of actual dry hide-powder taken to obtain the weight of wet hide-powder for 200 c.c. of solution.

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatin; 10 per cent. salt solution.

(10) *Tannin.*—The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

### III. ANALYSIS OF LIQUORS

(11) *Dilution.*—Liquors must be diluted for analysis, so as to give as nearly as possible 0.7 gramme solids per 100 c.c. of solution.

(12) *Total Solids.*—To be determined as in extract analysis.

(13) *Soluble Solids.*—To be determined as in extract analysis.

(14) *Non-tannins.*—To be determined by shaking 200 c.c. of solution with an amount of wet chromed hide-powder, containing 70 per cent. moisture, corresponding to an amount of dry hide-powder shown in the following table:—

TABLE LII

Tannin Range. Per 100 c.c.	Dry Hide-Powder. Per 200 c.c.
0.35 to 0.45 gramme.	9 to 11 grammes.
.25    „    .35    „	6.5   „    9    „
.15   „    .25    „	4   „    6.5   „
.00   „    .15    „	0   „    4    „

Solutions to be shaken for non-tannins as in extract analysis; 100 c.c. must be evaporated as in extract analysis.

### IV. EVAPORATION AND DRYING

(15) *Evaporation and Temperature.*—All evaporations and dryings shall be conducted in the form of apparatus known as the “Combined Evaporator and Dryer,” at a temperature not

less than 98° C. The time for evaporation and drying shall be sixteen hours.

(16) *Dishes*.—The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes, of not less than 2½ inches diameter nor greater than 3 inches in diameter.

#### V. DETERMINATION OF TOTAL ACIDITY OF LIQUORS

(17) (a) *Reagents*.—One per cent. solution of gelatin neutral to hæmatin. The addition of 25 c.c. of 95 per cent. alcohol per litre is recommended to prevent frothing. If the gelatin solution is alkaline, neutralise with tenth normal acetic acid, and if acid, neutralise with tenth normal sodium hydroxide.

(b) *Hæmatin*.—A solution made by digesting hæmatin in cold neutral 95 per cent. alcohol, in the proportion of ½ gramme of the former to 100 c.c. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

*Directions*.—To 25 c.c. of liquor in a cylinder that can be stoppered, add 50 c.c. of gelatin solution, dilute with water to 250 c.c., add 15 grammes of kaolin, and shake vigorously. Allow to settle for at least 15 minutes, remove 30 c.c. of the supernatant solution, dilute with 50 c.c. of water and titrate with tenth normal soda, using hæmatin solution as the indicator. Each c.c. tenth normal soda is equivalent to 0·2 per cent. acid as acetic.

On public analytical work by members of this Association, the fact that the Official Method has been used shall be so stated.

*Approximate Quantities of Tannin Materials to be Taken for Analysis*.—As a guide to the quantities of the various tanning materials to be taken in order to obtain solutions within the limits of strength laid down in the Official Method of tannin analysis, Professor Procter gives the following figures (grammes per litre):—

TABLE LIII

Barks, etc.		Extracts.	
Divi-divi . . .	9	Quebracho, solid . . .	6
Mangrove bark . . .	10	Cutch . . . . .	6
Valonia beard . . .	10 to 11	Mangrove, solid . . .	6 to 7
Mimosa bark . . .	10 „ 15	Chestnut, solid . . .	7
Valonia . . . . .	14 „ 15	Mangrove, liquid . . .	9
Myrobalams . . .	15		
Sumach . . . . .	15 „ 16	Quebracho, liquid . . .	9 to 13
Canigre . . . . .	15 „ 18	Gambier, cube . . . .	10
Quebracho wood . .	20 „ 22	Mimosa, D . . . . .	10 „ 12
Pistacia lentiscus .	20 „ 30	Hemlock . . . . .	10 „ 14
Oak bark . . . . .	30 „ 36	Gambier, block . . . .	12 „ 14
Pine bark . . . . .	32	Chestnut, liquid . . . .	14
Hemlock bark . . .	32 „ 36	Myrobalams . . . . .	16
Willow bark . . . .	36	Pine bark . . . . .	16
Chestnut wood . . .	45	Oak wood, sp. gr. 1·2 or over	18
Oak wood . . . . .	50 „ 100		
Spent tans . . . .	50 „ 100		

*Supplementary Notes on the Preceding Method. I. Apparatus used for the Exhaustion of Solid Tanning Substances. (a) Koch's Apparatus.*—This apparatus consists of a 200 c.c. flask with a wide neck, which should be of thin glass, and well tempered to stand the heat of the water bath. This flask is closed by a rubber cork traversed by two glass tubes; the first tube enters slightly inside the flask, the second dips to the bottom, enlarging slightly in the shape of a funnel. The extremities of these tubes are fitted with a piece of silk gauze so as to prevent the passage of solid particles. The flask may be dipped into a water-bath; the first tube may be put in communication by means of a tube fitted with india-rubber tubing, and a clip with a water reservoir placed at a height of 1.5 metres (5 feet). The second tube, likewise fitted with an india-rubber tube and clip to form a siphon, dips into a graduated litre flask. There is first introduced into the flask a layer of about 2 cm. of fine sand washed with acids, then the known weight of pulverised tanning substances is added, and the cork and its tubes inserted. There is no need to trouble about the disarrangement of the layers produced at this moment, because owing to its density the sand resumes its place as soon as water is introduced into the flask. Moreover, in the case of fibrous substances it is preferable to first fix the second tube after having raised the cork by gliding it along the tube; the sand is introduced and then the substance to be exhausted. When the filling is finished the cork is inserted and the whole firmly fixed or made fast either by means of string or by a clamp. When the water has acted sufficiently the clips are opened, the tannin liquor from the vessel is forced into the graduated flask and replaced by pure water, the clips are closed again and the exhaustion continued. It is even preferable to facilitate the passage of the liquor from the vessel into the flask, to add a third tube closed by a clip which is blown through after closing the first tube. The vessel can thus be completely emptied before filling it with pure water.

*(b) Procter's Apparatus.*—This apparatus is much more simple than the preceding, consisting essentially of a beaker which may be heated on the water-bath; into this vessel dips a reversed thistle funnel, the tube of which is bent twice at a right angle to form a siphon. The mouth of the funnel is closed by a piece of silk gauze and rests on the bottom of the dish. To the end of the tube a drawn-out piece of tube is joined. The bottom of the beaker is lined with sand, washed by acids, and above is laid the tanning substance to be exhausted. Water is added and heated to the desired temperature on the water-bath, and when the first exhaustion is judged sufficient the liquid is aspirated into another vessel.

(c) *Soxhlet's Apparatus*.—Some chemists use Soxhlet's apparatus for the extraction of tannin, but it is evident that this

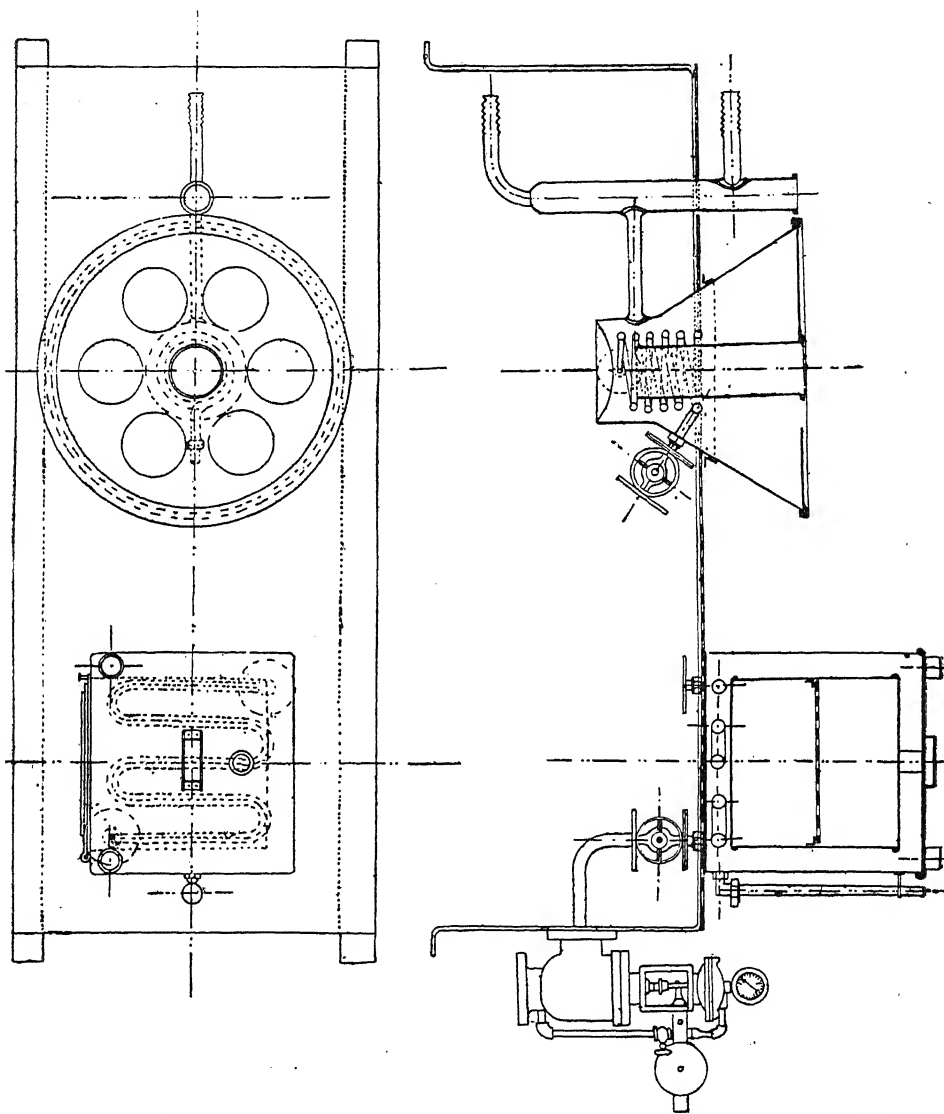


FIG. 118.—Water-bath for the estimation of soluble matter and non-tannins in the analysis of tanning substances (J. Noyer).

apparatus cannot be utilised for the application of the official method described above. In fact, in the Soxhlet tube, extrac-

tion is effected at 100° C., whilst, according to the preceding indications, the major portion of the tannin should be extracted first at a temperature below 50° C. The temperature of 100° C. should be reached only at the end of the process, and then for as short a time as possible.

II. *Influence of the Temperature of the Extraction on the Results in Assimilable Tannin.*—It has been seen in regard to the manufacture of extracts: (1) That there existed for each tanning substance a temperature at which the extraction yields the maximum of tannin, other things being equal. (2) If the operation be performed at increasing temperatures, higher than those which have just been quoted, larger and larger amounts of tannin are destroyed, besides it is the most soluble tannins, and consequently those which are dissolved at the outset, which are converted into inert compounds. (3) By prolonged ebullition the non-tannin extractive matter present in the vegetable tanning substances, which were originally insoluble, become soluble, and the more the ebullition is prolonged the more does the water become charged with such substances. The result evidently is that the proportion of soluble non-tannin matter is a function of the duration of heating and the number of the exhaustions with water. From the three preceding remarks it may be concluded that the results obtained in the analysis of the same tanning substance depend largely on the conditions under which its extraction is carried out. It is on that account that it was decided at the London Conference of 1897 that the exhaustion should be done at a temperature below 50° C., so as to extract the greater part of the tannin at a somewhat low temperature, and avoid, on the one hand, the solution of insoluble substances, and on the other hand the transformation of assimilable tannin into soluble non-tannin. After this first treatment, which removes the most soluble tannins, heat may be applied at 100° C. to terminate the exhaustion, without introducing any very important errors. It is to be hoped, however, that a future conference will define, in a still more precise manner, the conditions under which this operation should be carried out, so that analyses by different chemists might be comparable with each other.



## CHAPTER XI

### STATISTICS RELATING TO TANNING MATERIALS

THE following tables show the United Kingdom imports and re-exports of tanning materials for the years 1911-16:—<sup>1</sup>

TABLE LIV

	Quantities.					
	1911. Cwt.	1912. Cwt.	1913. Cwt.	1914. Cwt.	1915. Cwt.	1916. Cwt.
<i>Imports—</i>						
Gambier . . .	100,233	94,061	101,712	141,971	208,748	185,499
Extracts . . .	1,500,000	1,700,000	1,850,000	1,941,000	1,280,540	—
Myrobalams . . .	515,216	576,624	565,222	560,600	778,984	861,729
Valonia . . . .	248,093	287,810	346,092	361,453	142,456	134,349
Mimosa and other						
Bark . . . . .	650,834	572,901	892,054	846,276	761,623	572,891
Sumach . . . .	226,919	215,477	164,100	152,006	143,333	124,811
<b>Total . . . .</b>	<b>3,241,295</b>	<b>3,446,873</b>	<b>3,919,180</b>	<b>4,003,306</b>	<b>3,315,684</b>	<b>1,879,279</b>
<i>Re-exports—</i>						
Bark for tanning .	482,320	399,010	677,627	606,796	301,029	212,479
Extracts for tanning.	Entered by value only.					
Gambier . . . .	11,003	11,081	8,154	24,807	28,129	48,984
Cutch . . . . .	28,345	20,785	14,813	17,792	57,991	66,576
Myrobalams . . .	7,986	14,698	22,052	14,270	24,511	35,479
Sumach . . . . .	68,060	33,350	18,091	7,706	10,629	14,276
Valonia . . . . .	12,764	8,896	3,841	3,398	892	—
Tanning substances unenumerated .	1,779	201	7,579	3,147	8,382	7,971
<b>Total . . . .</b>	<b>612,257</b>	<b>488,021</b>	<b>752,157</b>	<b>677,916</b>	<b>431,563</b>	<b>385,765</b>
<b>Balance . . . .</b>	<b>2,629,038</b>	<b>2,958,852</b>	<b>3,167,023</b>	<b>3,325,390</b>	<b>2,884,121</b>	<b>1,493,514</b>

<sup>1</sup> *Leather Trades Year Book*, 1917-18.

TABLE LV

	Values.					
	1911. £	1912. £	1913. £	1914. £	1915. £	1916. £
<i>Imports—</i>						
Gambier . . .	140,744	136,704	142,026	174,253	306,698	416,983
Extracts . . .	739,329	844,998	922,600	970,283	1,920,801	3,309,660
Myrobalams . . .	188,844	162,646	176,855	162,941	292,297	499,629
Valonia . . .	121,227	152,186	164,208	171,921	101,922	167,117
Mimosa and other bark . . .	243,128	224,083	348,082	321,379	322,158	378,205
Sumac . . .	103,981	104,156	83,161	80,996	84,040	79,420
Total . . .	1,487,253	1,624,773	1,836,932	1,881,773	3,027,916	4,851,014
<i>Re-exported—</i>						
Bark for tanning . .	187,587	172,769	275,795	238,372	130,734	129,784
Extracts for tanning . .	28,142	28,825	32,056	39,004	721,255	1,135,317
Gambier . . .	14,340	15,647	14,833	29,828	44,202	120,742
Cutch . . .	35,073	24,236	18,833	22,098	87,503	147,058
Myrobalams . . .	2,491	4,531	6,371	5,232	12,055	26,797
Sumach . . .	31,115	17,139	8,805	3,952	6,146	9,420
Valonia . . .	5,886	4,260	2,706	1,987	673	—
Tanning substances unenumerated . .	894	152	3,832	1,550	4,983	6,621
Total . . .	305,528	267,559	363,231	342,123	1,007,551	1,575,739
Balance . . .	1,181,725	1,357,214	1,473,701	1,539,650	2,020,365	3,275,275

The following are the imports of tanning extracts into the United Kingdom for the years 1911-16 :—<sup>1</sup>

<sup>1</sup> *The Leather Trades Year Book*, 1917-18.

TABLE LVI

From	1911. £.	1912. £.	1913. £.	1914. £.	1915. £.	1916 £.
Austria-Hungary . . . .	75,853	85,923	58,260	24,855	—	—
Belgium . . . . .	11,663	17,519	18,955	10,630	—	—
France . . . . .	374,009	395,760	429,866	390,121	158,821	357,4
Germany . . . . .	30,905	20,606	25,747	16,968	—	—
Argentine Republic . . .	105,143	135,457	167,196	246,527	1,204,686	2,078,6
United States of America	32,473	45,177	46,028	77,640	404,827	785,6
Other Foreign Countries	21,836	28,695	46,038	55,894	17,621	11,7
Total Foreign Countries	715,642	815,680	880,157	930,807	1,834,909	3,233,4
Canada . . . . .	8,913	5,390	4,136	5,722	16,591	16,6
Other British Possessions	4,768	23,928	38,307	35,991	47,959	59,4
Total British Possessions	23,681	29,318	42,443	41,713	64,550	76,0
Total . . . . .	739,323	844,998	922,600	972,520	1,899,459	3,309,4

The following particulars of the various tanning materials used in the United States in the years 1900 and 1905 are taken from the census:—

TABLE LVII

	1900.		1905.	
	Used.	Value. \$.	Used.	Value \$
Wood, cords . . . . .	211,040	675,321	253,981	795,7
Ground and chipped woods, lb. .	12,690,037	201,931	9,999,906	95,2
Bark, tons . . . . .	99,587	502,853	103,119	948,9
Ground bark, lb. . . . .	27,028,000	149,365	38,001,017	249,1
Sumac leaves, tons . . . . .	8,333	150,259	4,456	93,5
Ground sumac, lb. . . . .	9,284,000	114,660	5,061,333	65,1
<i>Extracts—</i>				
Sumac, lb. . . . .	4,349,742	103,085	4,093,619	95,5
Hemlock „ . . . . .	26,011,714	563,591	18,833,450	406,6
Oak and chestnut, lb. . . . .	28,983,036	529,670	156,520,123	2,411,1
Palmetto „ . . . . .	1,050,000	20,000	1,740,000	34,8
Tanning liquors „ . . . .	16,144,292	405,659	44,418,929	1,704,2
Tannic acid „ . . . . .	1,326,515	149,662	5,165,500	200,1

According to the United States Census Bureau, December 1909, the total amount of tan bark and tannin extract used in the United States in 1908 was valued at \$21,361,719, and 1

imports and home production for 1907 and 1908 were as follows:—

TABLE VIII.—IMPORTS

	1907.		1908.	
	Quantity.	Value.	Quantity.	Value.
Number of tanneries . . . . .	583		622	
<i>Bark and Wood—</i>		\$		\$
Hemlock bark, cords . . . . .	6,193	27,786	8,877	43,789
Mangrove bark, tons . . . . .	20,699	426,439	15,190	310,745
Quebracho, „ . . . .	63,310	840,799	48,871	612,971
All other . . . . .	—	82,024	—	126,193
<i>Extract—</i>				
Quebracho, lb. . . . .	76,479,846	2,243,386	62,593,671	2,037,648
Sumac „ . . . . .	1,537,420	55,701	1,060,694	42,022
Myrobalam „ . . . . .	—	198,688	20,988,206	229,441
Totals . . . . .		3,874,803		3,402,809

TABLE LIX.—U.S. PRODUCTION

	1907.		1908.	
	Quantity.	Value. \$	Quantity.	Value. \$
<i>Tan Bark—</i>				
Hemlock cords . . . . .	815,840	7,016,915	810,231	7,203,206
Oak „ . . . . .	374,052	3,933,038	307,817	3,325,908
All other „ . . . . .	24,509	605,921	9,352	274,323
Totals . . . . .	1,214,401	11,555,874	1,127,400	10,803,437
<i>Extracts—</i>				
Hemlock, lb. . . . .	40,133,524	968,041	40,808,723	1,043,311
Oak „ . . . . .	30,830,291	639,388	21,705,775	460,124
Quebracho „ . . . . .	145,324,677	4,995,807	143,174,614	4,934,475
Chestnut „ . . . . .	134,819,100	2,560,007	146,818,963	2,853,045
Palmetto „ . . . . .	486,980	12,502	163,049	3,980
All others . . . . .	13,304,963	473,378	39,429,963	1,263,347
Totals . . . . .	364,899,535	9,649,673	392,101,087	10,558,282

*Total French Production, 1904.*—The total production of extract including that of Corsica reached in 1904 about 105,000 tons, representing a value of about 26,000,000 francs (about £1,040,000).

TABLE LX.—TANNIC ACID EXTRACT TRADE OF FRANCE, 1900-1903 (BOTH INCLUSIVE)

Country.	Imports from.				Exports to.			
	Net Weight in Kilos. <sup>1</sup>				Net Weight in Kilos. <sup>1</sup>			
	1900.	1901.	1902.	1903.	1900.	1901.	1902.	1903.
Britain	69,974	57,223	38,095	—	12,976,890	12,210,233	12,681,424	19,045,474
Holland	61,537	93,026	—	—	—	—	—	—
Germany	—	85,278	150,850	116,568	3,182,555	4,821,441	4,516,444	6,688,161
Belgium	881,460	137,391	321,315	196,526	6,171,819	5,629,341	6,438,218	7,963,784
Switzerland	118,842	108,418	122,436	118,273	680,214	557,036	648,289	637,331
Austria-Hungary	493,696	883,822	707,750	666,383	—	736,216	—	—
Spain	—	—	—	—	314,513	—	—	718,961
Italy	137,400	183,285	51,201	48,387	773,192	872,596	1,068,239	1,303,514
Roumania	—	—	—	—	—	—	667,572	—
Russia	—	—	—	—	476,527	1,347,269	1,986,038	1,057,057
U.S.A.	111,030	86,214	137,903	115,267	—	—	—	—
Argentina	—	—	30,082	42,331	—	—	—	—
Uruguay	—	—	—	32,315	—	—	—	—
Other countries	108,832	5,262	—	53,887	1,412,554	1,939,014	2,007,615	1,978,680
Algeria	—	—	—	—	24,782	37,744	38,265	11,240
Tunis	—	—	—	—	—	—	20,624	42,800
Martinique	—	—	—	—	27,619	—	—	—
Reunion	—	—	—	—	—	31,489	—	—
Other colonies	—	—	—	—	26,699	27,785	20,099	13,988
Yearly total	1,484,771	1,639,919	1,587,457	1,416,745	26,066,364	28,210,164	30,092,727	38,460,990
Yearly value (francs)	297,954	327,984	317,491	283,349	5,213,273	5,642,031	6,018,545	7,892,198

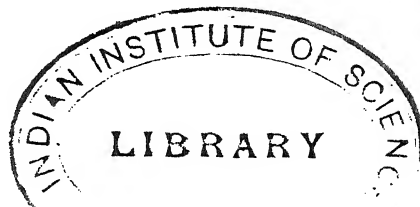
Value (francs).  
34,000  
8,887,000

Metric Quintals (100 kilos).  
19,625  
522,740

Year 1904, Importation  
" " Exportation  
The 1904 results as far as known are given as gross weights.

<sup>1</sup> By converting the numeration sign the farthest to the right into a decimal sign the weights are then expressed in metric tons of 2200 lb. and decimals thereof.

From the preceding figures for the three years since 1900 it is evident that the (French) imports only increased 37,000 francs, say, 9000 francs per annum (during 1903 there was actually a drop of 14,000 francs) whilst the exports have increased by 3,673,000 francs (£146,920) or 900,000 francs (£36,000) per annum, an increase which justifies, moreover, the impulse given to this eminently French industry.



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